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THE FREEZING-POINTS OF DILUTE AQUEOUS SOLUTIONS. III.

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THE following measurements were made during the winter months of 1895–96 in the Physical Laboratory of Princeton University.

The conditions under which the work was done were the same as during the preceding period of observation (winter, 1894–95), except that the lower and more nearly uniform temperature throughout the past winter made the maintenance of the room-temperature at about 3° C. much easier. In fact, the room-temperature rarely varied more than 0°.5 C. during an entire day.

This constancy of temperature has reduced the experimental error to one-half its former value, as appears from the fact that the average variation in a series of five entirely distinct and independent observations of the freezing-point of a given solution is now 0°.0005 C., while its former value was about 0°.001 C.

That the experimental errors are considerably lowered by this increased constancy of the room-temperature appears also in the fact that the successive observations of the freezing-point of water present less irregularity than in the previous work. (See Plate opposite p. 295, Fig. 3.)

This reduction of experimental error accounts for the greater regularity in the curves of molecular depressions in the region of

extreme dilution, as compared with the similar curves for the previous results. There seems to be no doubt that this reduction of the experimental error is due wholly to the greater constancy of the temperature of the mercury thread in the projecting stem of the thermometer. I think it now more probable than ever before, that a final degree of accuracy is to be looked for only under the condition of absolute constancy of the room-temperature at 0° C. On such days as permitted a close approach to this condition, I found the various manipulations were much more easily made and the different measurements more nearly approached exact concordance. It has not been found necessary to make the slightest change in the apparatus or method, and the measurements here to be submitted may thus be regarded as a mere continuation of those of the preceding winter (1894–95).

The present series of observations comprises the compounds named in columns 1 and 2 in the following table. In column (3) m denotes the concentration of the solution in gram-molecules per liter.

To avoid confusion the number of grams of the "water-free" compound per liter of the solution is given in column (4). In column (7) is given, under $S\frac{18°}{4°}$, the specific gravity of the solution whose concentration is found in the column which stands immediately before it. In addition, the table gives the name of the maker of the chemicals used and the particular process by which the original solutions were prepared.

The Chlorides, — Preparation of Solutions.

Lithium Chloride was prepared by treating lithium carbonate, which was obtained in a high state of purity from Merck & Co., with dilute HCl. The solution was then carefully neutralized, care being taken to expel all CO_2. The specific gravity of the solution was taken with a Mohr balance, and the solution diluted to approximate normal strength by use of Kohlrausch's tables of specific gravity.[1]

[1] Kohlrausch, Wiede. Ann. 6, p. 38, 1879.

TABLE I.

1 Compound.	2 Chemical formula.	3 m	4 Grams per liter of solution at 18° C.	5 Specific gravity.[1] Water at 4° C. = 1.	6 Electrical conductivity.[2] $K \cdot 10^6$. 18° C.	7 m	7 $s\frac{18°}{4°}$	8	9 Standard solution prepared.
Lithium chloride	$LiCl$	0.9917	42.13	1.0226	589	0.1983	1.0034	Prepared in laboratory	Kohlrausch tables
Calcium chloride	$CaCl_2$	0.5021	55.68	1.0438	635	0.2008	1.0170	" " "	" "
Strontium chloride	$SrCl_2$	0.4986	78.98	1.0672	633	0.1994	1.0264	Trommsdorff	" "
Stannic chloride	$SnCl_4$	0.250	64.98	$1.0486_{(15°)}$	195_0	0.200	1.0384	Eimer & Amend	Gerlach's tables
Nitric acid	HNO_3	1.0000	63.04	1.0324	278_5	0.2000	1.0054	Prepared in laboratory	Hulett's titration
Potassium hydroxide	KOH	1.0000	56.14	1.0481	170_0	0.2000	1.0091	" " "	" "
Sodium hydroxide	$NaOH$	1.0000	40.06	1.0418	145_2	0.2000	1.0079	" " "	" "
Potassium di-hydrogen phosphate	KH_2PO_4	0.333	45.38	1.0299	198	0.2000	1.0175	Eimer & Amend	Direct weighing
Di-sodium acid phosphate	Na_2HPO_4	0.2000	28.42	1.0260	—	0.2000	1.0260	Merck & Co.	" "
$NaNH_4HPO_4$	$NaNH_4HPO_4$	0.333	45.70	1.0345	282	0.200	1.0207	" "	" "
Tri-sodium phosphate(?)	Na_3PO_4(?)	0.33(?)	54.73	1.06	—	—	—	Prepared in laboratory	" "
Sodium silicate	Na_2SiO_3	0.523	64.08	1.0636	663	0.21	1.026	Trommsdorff	Kohlrausch tables[3]
Acetic acid	$C_2H_4O_2$	1.0000	60.01	1.0073	12	0.2000	1.0004	Merck & Co.	Hulett's titration
Oxalic acid	$(COOH)_2$	0.5000	45.00	1.0199	551	0.2000	1.0073	" "	Direct weighing
Succinic acid	$C_4H_6O_4$	0.4975	58.71	1.0167	17	0.1990	1.0060	Eimer & Amend	" "
Tartaric acid	$C_4H_6O_6$	0.9970	149.57	1.0653	87	0.1994	1.0122	Marquart	" "
Citric acid	$C_6H_8O_7$	0.9983	209.67	$1.0777_{(18°)}$	64	0.1997	1.0145	Merck & Co.	" "

[1] Temperature of solutions is 18° except when otherwise indicated.

[2] Conductivity with reference to mercury at 0° C.

[3] Kohlrausch, Zeit. Phys. Chem. XII., p. 773.

The specific gravity of this approximate solution was then exactly determined as described in former papers. This value is given in Table I., 5. The gram-molecular strength of the solution was easily computed by comparing this value with that given by Kohlrausch for a normal LiCl solution,[1] by means of his specific gravity tables. This gram-molecular strength of the original solution is given under (*m*) in Table I., 3. The diluter solutions whose freezing-points were to be measured were uniformly made by the use of most carefully marked flasks and pipettes. It needs perhaps to be said that these flasks and pipettes were marked for absolute volume when "dry." Careful rinsing insures the complete discharge of their contents into the measuring flasks.

Calcium Chloride.— An excess of $CaCO_3$ in the form of natural crystals of Iceland-spar was treated with dilute HCl, until the effervescence ceased. The whole was then boiled to expel CO_2 and the filtered solution carefully neutralized by addition of a slight quantity of HCl. It was then diluted to approximate normal strength, and finally its exact gram-molecular concentration was calculated as in the case of LiCl.

Strontium Chloride.—There happened to be a quantity of finely crystallized strontium chloride already in the laboratory (Trommsdorff, c.p.), which was used without recrystallizing. The gram-molecular strength of the final solution was determined as in the foregoing cases. It will be observed in Table I., 6, that the conductivity of this solution differs not inconsiderably from that given by Kohlrausch.[2] This is undoubtedly due to the fact that I did not recrystallize the salt. This error is, however, too slight to affect the measurements of the freezing-points.

Tin Chloride (stannic).—The salt was obtained from Eimer & Amend, and was not recrystallized. The normal solution was prepared by use of Gerlach's tables of specific gravity.[3] The temperatures of these particular tables of Gerlach are $\frac{15^\circ}{15^\circ}$.

The chlorides already studied in my former work are NaCl, KCl, NH_4Cl, $BaCl_2$, $MgCl_2$, and HCl.

[1] Kohlrausch, Leitfaden d. Physik, Leipzig, 1892, p. 404.
[2] Kohlrausch, Leitfaden, p. 404. [3] Hoffmann's Tabellen, Berlin, 1877, p. 130.

Observations on the first four have been extended so as to include solutions of greater concentration as follows: —

NaCl, $m = 0.70$,	NH_4Cl, $m = 0.70$,
KCl, $m = 0.70$,	$BaCl_2$, $m = 0.50$.

The following tables present the experimental results for the chlorides (Table II.). Column (1) contains the value of m for the various dilutions. The observed depression of the freezing-point is found in (2), while the molecular depression is found in (3).

In order to compute from the present data the molecular depression on the basis of gram-molecular concentration per 1000 grams of water, as Raoult and others are accustomed to do, one needs to know the specific gravity of the solution. Accordingly, this value is given for the solution near the concentration $m = 0.20$ in column 7, Table I. The difference between the value of the molecular depression so calculated and that given in the tables, which is based on gram-molecular concentration per liter of the solution, is altogether inappreciable in the more dilute solutions, and reaches its maximum value of 1.5 per cent in the case of tin chloride. I have accordingly omitted these second values of $\frac{\Delta}{m}$

Graphic Representation of Results.

The values of $\frac{\Delta}{m}$ as functions of m are represented in Fig. 2. (See Plate opposite p. 295.)

Ordinates represent values of $\frac{\Delta}{m}$, abscissæ, values of m. The scale here is the same as that adopted in the former papers.

Discussion of the Chlorides.

1. It will be remembered that a very striking fact is presented in the molecular depressions of the freezing-point by HCl and $MgCl_2$, as was indicated in the author's account of observations on these compounds;[1] namely, the fact that the molecular depression for each of these compounds reaches a pronounced minimum at about $m = 0.10$. It now appears that *all* the chlorides thus

[1] PHYSICAL REVIEW, III., p. 281.

TABLE II.

LITHIUM CHLORIDE.

[Values in parentheses obtained by interpolation.]

1 Gram-molecules per liter of solution (m).	2 Depression of freezing-point (Δ).	3 Molecular depression of freezing-point $\frac{\Delta}{m}$.	4 Theoretical value of Δ.	5 Theoretical value of $\frac{\Delta}{m}$	6 Difference $\Delta_{th}-\Delta_{ex}$.	7 Difference $\Delta_{th}-\Delta_{ex}$ in per cent of Δ_{ex}.
	deg.		deg.		deg.	
0.0099	0.0363	3.67	0.0358	3.61	−0.0005	−1.4
0.0198	0.0710	3.59	(0.0706)	(3.56_8)	0.0004	0.6
0.0496	0.1770	3.57	0.1730	3.48_7	0.004	2.3
0.0992	0.3520	3.55	0.3388	3.41_8	0.013	3.8
0.1983	0.7018	3.54	(0.6626)	(3.34)	0.039	5.6
0.4959	1.809	3.65	1.581	3.19	0.228	12.5
			CALCIUM CHLORIDE.			
0.0100	0.0513	5.13	(0.0510)	(5.10)	−0.0003	−0.5
0.0201	0.1013	5.04	(0.1000)	(5.00)	0.0013	1.3
0.0502	0.2437	4.85	0.238	4.74	0.006	2.5
0.1004	0.4823	4.80	(0.460)	(4.58)	0.022	4.5
0.2008	0.9718	4.84	(0.882)	(4.39)	0.090	9.3
0.5021	2.605	5.19	2.048	4.08	0.557	21.3
			STRONTIUM CHLORIDE.			
0.0100	0.0508	5.08(?)	(0.0495)	(4.95)	−0.0013	−2.6
0.0199	0.1015	5.10	(0.0966)	(4.83)	0.0049	4.8
0.0499	0.2445	4.90	0.234	4.68	0.011	4.5
0.0997	0.4834	4.85	(0.452)	(4.53)	0.031	6.4
0.1994	0.9608	4.82	(0.862)	(4.31)	0.099	10.3
0.4986	2.532	5.08	1.989	3.99	0.543	21.5
			TIN CHLORIDE ($SnCl_4$).			
0.01	0.1261	12.61				
0.02	0.2487	12.44	No data from which these values may			
0.05	0.5973	11.95	be calculated.			
0.10	1.1457	11.46				
0.20	1.968	9.84				

TABLE II. (*continued*).

Compound.	m	Δ	$\frac{\Delta}{m}$	Compound.	m	Δ	$\frac{\Delta}{m}$
		deg.				deg.	
NaCl	0.70	2.399	3.43	NH_4Cl . . .	0.70	2.384	3.41
KCl	0.70	2.346	3.35	$BaCl_2$	0.50	2.412	4.83

far examined, tin chloride excepted, manifest this same minimum, though in the case of NH_4Cl, NaCl, and KCl it is much less pronounced. To obtain a general survey of this fact, the curves of molecular depression for the various chlorides have been collected in Fig. 1, where the scale of values for m (abscissæ) has been decreased to one-half its value elsewhere in the plate in order to include the solutions of greater concentration. It is to be remarked that Arrhenius' observations on these chlorides quite generally exhibit this minimum value. Since these early observations lay no claim to a degree of exactness attained in the later methods, it is the more surprising that they so plainly reveal the existence of these minimum values which characterize the chlorides. Although Arrhenius called no attention to them, and evidently believed they were due to experimental errors, it is still difficult to understand why subsequent observers with more precise methods should have failed to find them. The existence of this minimum value in the case of the binary chlorides may be easily demonstrated with no other apparatus than an ordinary $\frac{1}{10}°$ thermometer and beaker glass.

2. The former division of the compounds into two groups, one containing univalent radicals, as LiCl, the other containing bivalent radicals, as $CaCl_2$, is confirmed by the new results here presented.

The characteristics of these two groups, as found in the former work, remain unaffected by the addition of this new material.

3. There is no evidence in any of the chlorides, or any other of the compounds examined, of any "kinks" in the curves of molecular depressions, save in the region of extreme dilution,

where they are so small as to be best explained by experimental errors.

It may be safely said, now that I have examined some thirty-five characteristic compounds, that the existence of definite "Hydrates" at particular concentrations is not indicated by the changes in the freezing-point which attend changes in the dilution of the solution.

Bearing of these Results on the Dissociation Theory.

In the table of results for the chlorides, and in the subsequent tables for other compounds, are found the theoretical values of the depressions of the freezing-point, and the theoretical values of the molecular depressions, respectively. These values are based on Kohlrausch's value for $\frac{\mu_z}{\mu_\infty}$. In column (6) is found the difference between the theoretical and observed value of the depressions, while in (7) this difference is expressed in per cents of the total observed value. It thus appears that the observed values are higher than the theoretical. The differences, however, in the region of extreme dilution in the cases of LiCl and $CaCl_2$ are surprisingly small. In case of $SrCl_2$ the difference is very great, the observed depression being 0°.0013 C. higher than the theoretical value, and the observed value is certainly too low, judging from the curve of the molecular depressions as exhibited in Figs. 1 and 2.

It needs to be remarked that the molecular depressions calculated on the basis of the dissociation theory show no minimum value. This accounts for the enormous departure of the observed from the theoretical value in the region of greater concentration.

The case of tin chloride needs separate discussion.

First, it is to be observed that the depressions are much more than twice as large as those produced by any other chloride in the same concentration. While it is impossible to compute the theoretical value of the depression on the basis of the dissociation theory, since measurements on the conductivity of these solutions are wanting, it is, however, a striking fact that if it be *assumed* that the salt at the concentration $m = 0.01$ be *completely* dissociated, and that each molecule splits up into the maximum number of

five parts, Sn–Cl–Cl–Cl–Cl, we would then have for the molecular depression only 5 × 1.89 or 9.45, while the observed value is 12.61. Obviously the depression is not to be explained in this way. It however suggests itself that the $SnCl_4$ does not exist at all in aqueous solutions, but that it assumes at once the properties of a mixture of $SnCl_2$ and 2 HCl, in solution. No value for the depression of the freezing-point by $SnCl_2$ has been found; but assuming that it is about that of $CdCl_2$ and $ZnCl_2$, as observed by Jones, *i.e.* 5.20, and taking the observed value for HCl, *i.e.* 3.61, we have for the depression due to $SnCl_4$, 5.20 + 2(3.61), or 12.42. This is very nearly the observed value. It should be said that many vain attempts were made to prepare solutions of $SnCl_2$, sufficiently free from $SnCl_4$, to enable the freezing-points to be measured.

The purpose was to measure the depressions in a solution of $SnCl_2$ at $m = 0.01$, and then add in succession a $\frac{1}{100}$ gram-molecule of HCl. Thus measurements would be made on

$$\begin{aligned} &SnCl_2, && m = 0.01,\\ &SnCl_2 + 1\ HCl, && m = 0.01,\\ &SnCl_2 + 2\ HCl, && m = 0.01,\\ &SnCl_2 + 3\ HCl, && m = 0.01, \end{aligned}$$

as was done in the cases of the phosphates, p. 288. This would have decided experimentally whether the suggestion just made in regard to the nature of $SnCl_4$ in solution is tenable. I hope to return to this difficulty in the near future. It may be well to call attention here to the great importance of exact measurements of the electrical conductivity of this salt, together with that of the various phosphates and the dilute solutions of $MgCl_2$ and NH_4NO_3 for the purpose of obtaining experimental values for the "degree of dissociation," $\frac{\mu_x}{\mu_\infty}$.

The Sodium and Potassium Hydroxides, Nitric Acid, and Sodium Silicate.

The materials used in the first three cases were those prepared in a high degree of purity for the purpose of determining their specific gravity and electrical conductivity.[1] The great care taken

[1] Loomis, PHYSICAL REVIEW, IV., 1896, p. 252.

TABLE III.

POTASSIUM HYDROXIDE.

[Values in parentheses obtained by interpolation.]

1 m	2 Δ	3 $\frac{\Delta}{m}$	4 Δ theoretical.	5 $\frac{\Delta}{m}$ theoretical.	6 Δth-Δexp	7 Δth-Δexp in per cents of Δexp.
	deg.		deg.		deg.	
0.0100	0.0343	3.43	0.0371	3.71	+0.0028	+ 8.1
0.0200	0.0689	3.45	(0.0738)	(3.69)	0.0049	7.1
0.0500	0.1719	3.44	0.1825	3.65	0.0106	6.1
0.1000	0.3426	3.43	0.360	3.60	0.017	5.0
0.2000	0.6860	3.43	(0.714)	(3.57)	0.028	4.1

SODIUM HYDROXIDE.

0.0100	0.0328	3.28(?)	0.0366	3.66	+0.0038	+11.6
0.0200	0.0691	3.46	(0.0724)	(3.62)	0.0033	4.7
0.0500	0.1727	3.45	0.1765	3.53	0.0038	2.2
0.1000	0.3414	3.41	0.350	3.50	0.0039	1.1
0.2000	0.6814	3.41	(0.696)	(3.48)	0.0015	0.2

NITRIC ACID.

0.0100	0.0350	3.50	0.0373	3.73	+0.0023	+ 6.6
0.0200	0.0712	3.56	—	—	—	—
0.0300	0.1059	3.53	0.1107	3.69	0.0048	4.5
0.0500	0.1754	3.51	0.1835	3.67	0.0081	4.6
0.1000	0.3496	3.50	0.363	3.63	0.013	3.7
0.2000	0.6959	3.48	(0.720)	(3.60)	0.020	2.8

SODIUM SILICATE.

0.0105	0.0676	6.46				
0.0209	0.1339	6.41				
0.0523	0.3068	5.87		No experimental data.		
0.1046	0.5533	5.29				
0.2092	0.9785	4.68				
0.5230	2.087	3.99				

to purify these materials was wholly unnecessary so far as the determination of their freezing-points was concerned, but as the material was at hand it was made use of for the present purpose.

The sodium silicate, Na_2SiO_3, was Trommsdorff's c.p. salt and was not recrystallized. It yielded a perfectly clear solution without filtering. It was reduced to normal solution by using Kohlrausch's values of specific gravity.[1]

The graphic representation of these results is found in Fig. 1. It is to be observed that the molecular depression for KOH, NaOH, and HNO_3, as exhibited in column (3), varies very little with the concentration, as has been found also to be the case with HCl. It is to be noted that the values for $m = 0.01$ in each instance are evidently too low and indicate experimental errors which reach, at least in the case of nitric acid, 0°.0006.

The value for NaOH, $m = 0.01$, I am unable to explain. The measurements were twice repeated, making in all thirteen entirely distinct observations on this solution. The average of all was 0°.0325. The value here given, 0°.0328, belongs to the same series to which the other measurements belong, and for this reason was taken. The error, I think, cannot be referred to possible errors of observation. It seems to be connected in some way with the solution. It is also difficult to believe that the conversion of the NaOH and KOH into the carbonates by the CO_2 of the air would be sufficient to account for the marked irregularity and for the seemingly low values throughout this region of greater dilution. The present method permits no experimental answer to this question.

Sodium Silicate. — The molecular depressions are very great, and the rate of decrease with increase in concentration, as in the case of $SnCl_4$, is enormous. Thus, while it is 6.46 at $m = 0.0105$, it has fallen to 3.99 at $m = 0.523$. It is not without interest to note that the *complete* dissociation of this salt in the solution $m = 0.0105$, provided each molecule splits into three parts after the analogy of Na_2SO_4, would still require the theoretical value to be only 3×1.89, or 5.67, which is much less than the observed value.

It seems probable that, as in the case of $SnCl_4$, the aqueous

[1] Kohlrausch, Zeit. Phys. Chem. XII., 1893, p. 774.

solution of Na_2SiO_3 has the properties of a mixture of NaOH and SiO_2 where the presence of the SiO_2 seems to lessen the degree of dissociation of the NaOH. The results of Kohlrausch's observations on the electrical conductivity seem to point to the same conclusion.

This point should receive a more careful study than I have thus far been able to give to it.

The Phosphates.

TABLE IV.

KH_2PO_4.			Na_2HPO_4.		
1 m	2 Δ	3 $\frac{\Delta}{m}$	1 m	2 Δ	3 $\frac{\Delta}{m}$
	deg.			deg.	
0.01	0.0358	3.58	0.01	0.0499	4.99
0.02	0.0720	3.60	0.02	0.0969	4.85
0.05	0.1740	3.48	0.05	0.2304	4.61
0.10	0.3365	3.37	0.10	0.4345	4.35
0.20	0.6434	3.22	0.20	Beyond limit of solubility at 0° C.	
$Na(NH_4)HPO_4$.			Na_3PO_4(?).		
0.01	0.0495	4.95	0.01	0.0715	7.15
0.02	0.0956	4.78	0.02	0.1369	6.85
0.05	0.2260	4.52	0.05	0.3048	6.10
0.10	0.4242	4.24	0.10	0.5661	5.66
0.20	0.7817	3.91	0.20	Not observed.	

Preparation of Solutions.

The KH_2PO_4 (Eimer & Amend, c.p.) was carefully recrystallized, and after continued drying at 100° C. the necessary amount was weighed and made into a normal solution ($m = \frac{1}{3}$). Mr. Sill of the Princeton Chemical Laboratory found by the determination of the salt as $Mg_2P_2O_7$ that there were 45.06 g. of KH_2PO_4 per liter of the solution instead of 45.38 g.; thus the solution was apparently 0.7 per cent too weak. As this difference could be due to impurity of the salt as well as to the failure to completely

dry the salt, I have not ventured to make any correction, and the results must be looked upon as affected with an error of 0.7 per cent.

The Na_2HPO_4 (Merck & Co., c.p.) was carefully recrystallized, and after heating at 120° C., until the weight became constant, the necessary amount was reduced to a normal solution by direct weighing. Mr. Sill's analysis showed that a liter of the solution, $m = 0.20$, contained 28.45 g. instead of 28.42 g. The solution was thus apparently 0.1 per cent too strong. This error is less than the probable error of the analysis, and the Na_2HPO_4 solutions may be looked upon as exact.

The $NaNH_4HPO_4$ (Merck & Co., c.p.) was recrystallized. It was dried with filter paper and finally in the air at a temperature a little above room-temperature.

Mr. Sill's analysis of the final solution, $m = \frac{1}{3}$, showed that it contained per liter 45.45 g. instead of 45.70 g., which is required for the solution, $m = \frac{1}{3}$. It was thus 0.55 per cent too weak. For the same reason as that given in the case of KH_2PO_4, no correction was applied to the results, though it is likely that the error here is wholly due to lack of complete drying of the salt.

The Na_3PO_4 was prepared in the laboratory by making a solution of molecular equivalents of Na_2HPO_4 and NaOH, taking care that an excess of NaOH was present. The solution was then evaporated to the point of crystallization. The abundant crop of crystals was then dissolved in one-half its weight of boiling water and left to recrystallize. The crystals thus prepared are small hexagonal prisms with jagged ends. These crystals were then dried at 120° C. to constant weight. The resultant compound should be Na_3PO_4, H_2O. The analysis of many solutions prepared on the basis of this formula for the dried salt and $Na_3PO_4 + 12H_2O$ for the crystals themselves gave me no confidence that the solutions could be looked upon as having more than a rough approximation to their supposed strength. Mr. Hulett made a very careful series of analyses of the crystals and found a very wide departure from the formula, $Na_3PO_4 + 12H_2O$. Time did not permit a final solution of the difficulty. The matter deserves a thorough study from the chemical side.

Discussion of Results for the Phosphates.

The depressions of the freezing-point, caused by phosphoric acid, H_3PO_4, are much less than those caused by the groups of compounds containing univalent and bivalent radicals, and this is the more surprising since phosphoric acid contains a trivalent radical.

For the purpose of examining into this matter more closely, I undertook to measure the freezing-points of the present series of phosphates.

1. The first fact which appears from the results is that the phosphates are entirely unlike the phosphoric acid and differ still more among themselves.

2. In proportion as the hydrogen of phosphoric acid is replaced by a univalent metallic radical, the depression of the freezing-point is increased. See curves for H_3PO_4, KH_2PO_4, Na_2HPO_4, and Na_3PO_4. (Fig. 2.)

3. If we assume that in the case of H_3PO_4 the molecule splits up into H and HPO_4, we may calculate the freezing-points on the basis of the dissociation theory.

The theoretical values so obtained are given in column (4), while in (2) are found the observed values taken from former measurements. The agreement here exhibited makes our assumption fairly probable that in the process of dissociation only a single atom of hydrogen is "split off."

TABLE V.

H_3PO_4.

1 m	2 Δ	3 $\frac{\Delta}{m}$	4 Δ_{th}	5 $\Delta_{th}-\Delta_{exp}$
	deg.		deg.	
0.01	0.0282	2.82	0.0296	+0.0014
0.02	0.0536	2.68	0.0552	0.0016
0.05	0.1245	2.49	0.1275	0.0030
0.10	0.2358	2.36	0.2400	0.0040
0.20	0.4498	2.25	0.4580	0.0082

It is to be remarked further that the degree of dissociation is much smaller than in the case of any inorganic compound so far examined, being only 56 per cent in the solution $m = 0.01$. Kohlrausch value for μ_∞ is assumed (110).

4. Passing now to the KH_2PO_4, where we have one H atom replaced by K, we find that the depressions produced belong to the group, KCl, NaCl, etc., and it at once suggests itself that with this salt as with all members of this group the molecule splits into two parts, in this case K and H_2PO_4, and that the degree of dissociation is about the same as for other potassium salts of the group.

Unfortunately, no measurements on the conductivity of KH_2PO_4 in extreme dilution have been made, so far as is known to the writer.

5. The replacement of a second atom of hydrogen by a metallic atom, as for example in the case of the two phosphates, Na_2HPO_4 and $NaNH_5HPO_4$, at once brings us into the second group, *i.e.* into the group of electrolytes which contain bivalent radicals, as K_2SO_4, $BaCl_2$, etc.

In this group the dissociation of the molecule is said to be into three parts, and the degree of this dissociation is on the average about 80 per cent in the solutions $m = 0.01$. Assuming the dissociation to be into three parts, namely, Na–Na–HPO_4, we are able to compute from the present data the degree of dissociation by the formula $\frac{\Delta}{m} = 1.89\ (1 + 2\delta)$, in which δ is the degree of dissociation. In this particular case, Na_2HPO_4, the value of δ is accordingly

$$\frac{0.0499}{0.01} = 1.89\ (1 + 2\delta),\ \text{or}\ \delta = 0.82.$$

For Na_2HPO_4 the degree of dissociation in the solution $m = 0.01$ is thus 82 per cent. Values for the electrical conductivity of this salt in solution are not yet known, and hence it is not possible to verify this result at present.

Replacing now the *third* H atom with Na, we have Na_3PO_4, and the observed depression for the solution $m = 0.01$ becomes 0°.0715. To account for this very great depression, the disso-

ciation theory requires that the salt be dissociated 93 per cent, each dissociated molecule yielding four parts. Here, however, as in the other cases, no electrical conductivity measurements have as yet been made.

For the sake of inquiring as closely as possible into the interesting matter presented by these phosphates, observations were made on the freezing-points of various mixtures of Na_2HPO_4 and NaOH solutions. The results are given at the end of the following table. The results for H_3PO_4 and the other phosphates under discussion are also found in the same table. The coefficients indicate the number of $\frac{1}{100}$ gram-molecules of the respective constituents in the solutions.

1	2 Depressions.	3 Successive differences.	1	2 Depressions.	3 Successive differences.
	deg.			deg.	
1 H_3PO_4	0.0282		1 Na_2HPO_4 + 2 NaOH	0.0995	0.0289
1 KH_2PO_4	0.0358	0.0076			
1 Na_2HPO_4	0.0499	0.0141	1 Na_2HPO_4 + 3 NaOH	0.1279	0.0284
1 Na_3PO_4	0.0715	0.0216			
1 Na_2HPO_4 + 1 NaOH	0.0706	—			

The successive differences which the series presents is not without interest. Assuming that in place of the salt KH_2PO_4 we had NaH_2PO_4, and that the depression due to the sodium salt is sensibly the same as that of the potassium salt,[1] then we observe (see table) that the addition of the first atom of Na increases the depression by 0°.0076, the second by 0°.0141, the third by 0°.0216. We have now reached the compound Na_3PO_4, to which the 1 NaH_2PO_4 + 1 NaOH is seen to be equivalent, at least, so far as the limits of accuracy of the latter solution require.

The further addition of 1 NaOH, as in the solution, 1 Na_2HPO_4 + 2 NaOH, which may be looked upon as equivalent to 1 Na_3PO_4 + 1 NaOH, increases the depression by 0°.0289. Thus far the

[1] My attempts to prepare solutions of NaH_2PO_4, which could be found by analysis to be sufficiently accurate, have thus far failed. All analogy, however, seems to allow the assumption which is made above.

successive differences appear, on the average, to be successive multiples of 0°.0073. The further addition of 1 NaOH, as appears in 1 Na_2HPO_4 + 3 NaOH, which is equivalent to Na_3PO_4 + 2 NaOH, is attended by about the same increase as that caused by the addition of the preceding molecule of NaOH, *i.e.* 0°.0284. Thus it would seem probable that the relation of the sodium atom to the rest of the molecule in the series of compounds examined is less and less close as the number of sodium atoms increases, and this fact may be sufficient ground on which to account for the progressive alkaline properties of this series of salts. I regret that these relations did not present themselves until the work was in preparation for publication (May–June), and thus no farther observations could be made. I wish again to emphasize that the results for Na_3PO_4 are certainly affected by a very large error, perhaps amounting to 7 per cent. I have no means, at present, of knowing in which direction this error lies. My only apology for presenting the results is the fact that even so large an error as this, either + or −, would not affect the essential nature of the interesting relations which the present study of the phosphates has brought to light. The examination of this question from the standpoint of electrical conductivity is desirable, since it appears that the dissociation theory would here encounter some very decisive tests.

The Organic Acids. (*Acetic, Oxalic, Succinic, Tartaric, and Citric.*)

The Preparation of the Solutions. — The acetic acid was reduced to normal strength by titration with the standards used in the preparation of the solutions previously described.[1] The preparation of the oxalic acid is described in the same connection. The succinic, tartaric, and citric acids were obtained from the makers in as high a degree of purity as they furnish them, and after drying as thoroughly in each case as their nature would permit, they were reduced to solutions of desired strength by direct weighing. They were then each titrated and corrected in accordance with the result of the titration, on the assumption that their having less than the supposed strength was due to the difficulty of

[1] Loomis, PHYSICAL REVIEW, IV., 1896, p. 252.

completely drying them. The corrections are relatively very small, even in the case of succinic acid, where they amount to 0.5 per cent.

The results are given below in tabular form, and graphically, near the bottom of Fig. 2.

TABLE VI.

ACETIC ACID, $C_2H_4O_2$.

$\mu_{20} = 364$.

1 m	2 Δ	3 $\frac{\Delta}{m}$	4 Δ theoretical.	5 $\frac{\Delta}{m}$ theoretical.	6 Δth-Δexp	7 Δth-Δexp in per cents of Δexp.
	deg.		deg.		deg.	
0.0100	0.0196	1.96	0.0196	1.96	+0.0000	+0.0
0.0200	0.0375	1.88	(0.0388)	(1.94)	0.0013	3.5
0.0300	0.0559	1.86	0.0579	1.93	0.0020	3.6
0.0500	0.0928	1.86	0.0960	1.92	0.0032	3.4
0.1000	0.1855	1.86	0.191	1.91	0.0055	3.0
0.2000	0.3732	1.87	0.382	1.91	0.0090	2.4
0.3000	0.5629	1.88	—	—	—	—
0.5000	0.9378	1.88	—	—	—	—
1.0000	1.886	1.89	1.90	1.90	0.01	0.5

OXALIC ACID, $(COOH)_2$.

$\mu_{20} = 363(?)$.

0.0100	0.0328	3.28	(0.0351)	(3.51)	+0.0023	+7.0
0.0200	0.0640	3.20	(0.0676)	(3.38)	0.0036	5.6
0.0500	0.1519	3.04	—	—	—	—
0.1000	0.2848	2.85	—	—	—	—
0.2000	0.5329	2.66	—	—	—	—

SUCCINIC ACID, $C_4H_6O_4$.

$\mu_{20} = 356$.

0.0100	0.0202	2.02	0.0204	2.04	+0.0002	+1.0
0.0199	0.0391	1.96	0.0398	2.00	0.0007	1.8
0.0498	0.0965	1.94	0.0976	1.96	0.0011	1.1
0.0995	0.1876	1.89	—	—	—	—
0.1990	0.3751	1.89	—	—	—	—

TABLE VI. (*continued*).

TARTARIC ACID, $C_4H_6O_6$.

$\mu_\infty = 356$

1 m	2 Δ	3 $\frac{\Delta}{m}$	4 Δ theoretical.	5 $\frac{\Delta}{m}$ theoretical.	6 Δth-Δexp	7 Δth-Δexp in per cents of Δexp.
	deg.		deg.		deg.	
0.0100	0.0234	2.34	(0.0239)	(2.39)	+0.0005	+2.1
0.0200	0.0435	2.18	(0.0454)	(2.27)	0.0019	4.4
0.0499	0.1042	2.09	(0.1070)	(2.14)	0.0028	2.7
0.0997	0.2018	2.02	—	—	—	—
0.1994	0.3993	2.00	—	—	—	—
			CITRIC ACID, $C_6H_8O_7$.			
0.0100	0.0226	2.26				
0.0200	0.0424	2.12				
0.0499	0.1029	2.06		No	data.	
0.0998	0.1999	2.00				
0.1997	0.3978	1.99				

In computing the theoretical values for the depressions, the Kohlrausch values for electrical conductivity are used in the case of acetic acid. In other cases the Ostwald[1] measurements are used. In all cases Ostwald's value for μ_∞ was assumed as the most probable. This value is given at the top of the separate tables. No electrical measurements, so far as is known to me, have been made on citric acid. It should be said, perhaps, that the particular acids examined were chosen for the sole reason that they may be had in a high state of purity and are easily made into solutions of exact molecular strength.

This series of organic acids is chiefly interesting on account of the relation which is presented by them between the observed depressions and those required by the dissociation theory.

It appears that in the case of acetic, succinic, and tartaric acids, the agreement between the observed and the theoretical values for extreme dilution is so nearly exact that, barring experimental errors, it may be regarded as complete. Further, these theoretical values of the depressions indicate that the Ostwald values for μ_∞ are

[1] Ostwald, Zeit. Phys. Chem., III., 1889, pp. 174, 281, 371.

very probable, although in the case of acetic acid the experimental values for the electrical conductivity as found by Kohlrausch would not perhaps warrant the assumption of so high a value.

The exception presented by oxalic acid is not to be overlooked. This acid presents difficulties in other directions, as well as in the present instance, and it may happen that fuller knowledge of its nature may be able to reconcile the "theoretical" with the observed depressions of the freezing-point.

The Constancy of the Thermometer.

In conclusion I wish to submit the entire series of observations on the zero point of the $\frac{1}{100}°$ thermometer, which were made during the period of the present measurements.

This thermometer has been in use four years. It has been kept at room-temperature except during the period of the measurements, when it is kept constantly within the limits, $-3°$ and $+1°$ C.

In the following table the observed zero points are given in (4), and the values when corrected to 760 mm., and a room-temperature 0° C. are given in (5).

1 1896.	2 Barometer.	3 Room-temperature.	4 Observed zero point.	5 Zero point corrected.
		deg.	deg.	deg.
Jan. 6	769.9 mm.	0 C.	0.0438	0.0422
7	766.6	0	0.0439	0.0428
20	763.3	5	0.0468	0.0439
22	762.0	6	0.0469	0.0438
29	765.6	6	0.0475	0.0438
Feb. 3	754.6	5	0.0457	0.0442
10	753.1	5	0.0458	0.0447
13	754.4	5	0.0460	0.0446
17	770.1	0	0.0451	0.0433
19	749.3	5	0.0454	0.0449
22	766.1	2	0.0456	0.0437
26	750.3	2	0.0440	0.0447
Mar. 3	751.6	3	0.0447	0.0447
4	753.1	3	0.0447	0.0445
5	753.9	5	0.0465	0.0452
11	749.1	4	0.0450	0.0449
12	747.8	4	0.0449	0.0452
16	756.2	4	0.0458	0.0445
17	756.4	5	0.0466	0.0449

The results are graphically represented in Fig. 3. Ordinates represent thermometer readings, abscissæ time of observations.

The scale is so chosen that the observed changes in the thermometer readings are magnified 125-fold. In order to facilitate comparison between the observed course of the zero-point and what it would have been in case it had made a strictly uniform rise of 0°.0022 during the period, a straight line has been drawn from 0°.0428 to 0°.0450. We observe, first, that the initial reading is 0°.0422. The last reading of the preceding winter was 0°.0417.

It thus appears that during the nine months of rest the zero of the thermometer remained constant. The total rise during the present period is about 0°.002 C.; during the preceding winter it was a little more than 0°.002 C. Further, it is noticeable that the course of the observed zero point is much less of a "zig-zag" than in former periods of use. This, I think, is due to a reduction of the experimental error of the method and to a greater constancy of the thermometer itself, due to its age and continued use.

The sharp changes between Feb. 13 and Feb. 22 must, I think, be referred to the thermometer itself and not to experimental errors, since the series of depressions which were measured on these particular days indicate no corresponding errors. The HNO_3 series was measured on Feb. 19, when the zero point seems to be too high. While this particular series of observations show unusually large experimental errors, these errors seem to suggest that the zero point was too low rather than too high. The other zero points in this period of marked variation of the thermometer were made in connection with solutions which are not yet ready for publication, which, however, show no cause for assuming that the zero points were erroneously determined. This matter will be noticed fully at the proper time.

Summary of Results.

1. The method developed in 1893 has been used, with no change whatever (except an enlargement of the "freezing-tube"), to de-

termine the depression of the freezing-point for the following solutions: —

$LiCl$, $CaCl_2$, $SrCl_2$, $SnCl_4$,
HNO_3, KOH, $NaOH$,
KH_2PO_4, Na_2HPO_4, $Na(NH_4)HPO_4$, Na_3PO_4,
Na_2SiO_3,
$C_2H_4O_2$, $(COOH)_2$, $C_4H_6O_4$, $C_4H_6O_6$, $C_6H_8O_7$.

2. It has been found that the average variation in a series of five entirely independent determinations of the freezing-point of a solution is now 0°.0005, or about half its former value. This indicates a reduction of the experimental errors, and this indication is confirmed by the greater regularity of the results in the region of extreme dilution. It is thought that this decrease in the experimental error is due wholly to a greater constancy of the room-temperature.

3. The observations on the four chlorides of the present series, together with additional observations on the five chlorides previously studied, establish the fact that the *molecular depression of the freezing-point for all chlorides reaches a minimum value.* This depression is very pronounced for the binary chlorides. See Fig. 1.

$SnCl_4$ yields such enormous depressions that the measurements could not be carried far enough to establish any conclusion in this regard. There is no reason, however, for believing that this chloride would not also reveal a minimum in the molecular depression if the measurements had been extended into the region of greater concentration.

4. Tin chloride in extreme dilution produces a molecular depression of 12.61. This is more than five times the van't Hoff constant (1.89). The hypothesis of Arrhenius fails thus to explain the depression, since the greatest possible number of "active molecules" which a molecule of $SnCl_4$ could yield would be *five*, and so the maximum molecular depression which this salt could produce would be 5×1.89, or 9.45. The observed molecular depression, however, is 12.61, at $m = 0.01$. It may be suggested that $SnCl_4$ in solution possesses the properties of a mixture

of $SnCl_2$ and 2 HCl. If this be so, the molecular depression would be about 12.42. This is not far from the observed result. The strong acid reaction of solutions of $SnCl_4$ favors the suggestion.

5. The study of the phosphates makes it probable that H_3PO_4 in aqueous solution is dissociated simply into two parts, — H and H_2PO_4.

This appears from the fact that its salt, KH_2PO_4, gives a depression which belongs to the first group, namely, to the class of electrolytes which yield two parts in the process of dissociation (NaCl, KCl, etc.). Thus the *salt* probably splits into K and H_2PO_4, and this points to the conclusion that the acid behaves similarly.

Further, it appears that the successive introduction of a univalent metallic radical into a salt of phosphoric acid increases the depression by a constant amount for each radical so added. This would be explained on the basis of the dissociation theory by saying that the introduction of each metallic radical increases by one the number of parts into which the molecule is dissociated, and causes no essential change in the *degree* of dissociation.

Thus in KH_2PO_4 there are two parts, K and H_2PO_4,
in Na_2HPO_4 there are three parts, Na–Na–HPO_4,
in Na_3PO_4 there are four parts, Na–Na–Na–PO_4.

6. Sodium silicate, Na_2SiO_3, presents the same difficulty as $SnCl_4$, *i.e.* the depression is much greater than the simple hypothesis of Arrhenius can account for.

7. The organic acids — acetic, oxalic, succinic, tartaric, and citric — exhibit the characteristics of the electrolytes, and not those of the non-electrolytes. The only exception is acetic acid, which in the more concentrated solutions behaves exactly like the non-electrolytes; namely, beyond $m = 0.10$, the molecular depression *increases uniformly* with the concentration.

8. A comparison of the experimental results with those required by the hypothesis of van't Hoff and Arrhenius shows that in the case of LiCl and $CaCl_2$ the agreement is practically complete. A most striking agreement is also presented by acetic, tartaric, and succinic acids.

The agreement is fairly good in the case of $SrCl_2$.

On the contrary HNO_3, KOH, and NaOH deviate very widely from the "theory." The differences between the observed values and those required by the hypothesis of Arrhenius are 8–11 per cent for the most dilute solutions. The fact that these differences become very small in the region of greatest concentration suggests the existence of some unknown source of error peculiar to the solutions.

In the remaining cases, $SnCl_4$, citric acid, and the salts of phosphoric acid, no measurement of the electrical resistances have been made, and thus no data are at hand for computing the theoretical values of the depressions.

These measurements are much needed, together with those for the extremely dilute solutions of $MgCl_2$ and NH_4Cl.

PHYSICAL LABORATORY, PRINCETON UNIVERSITY.

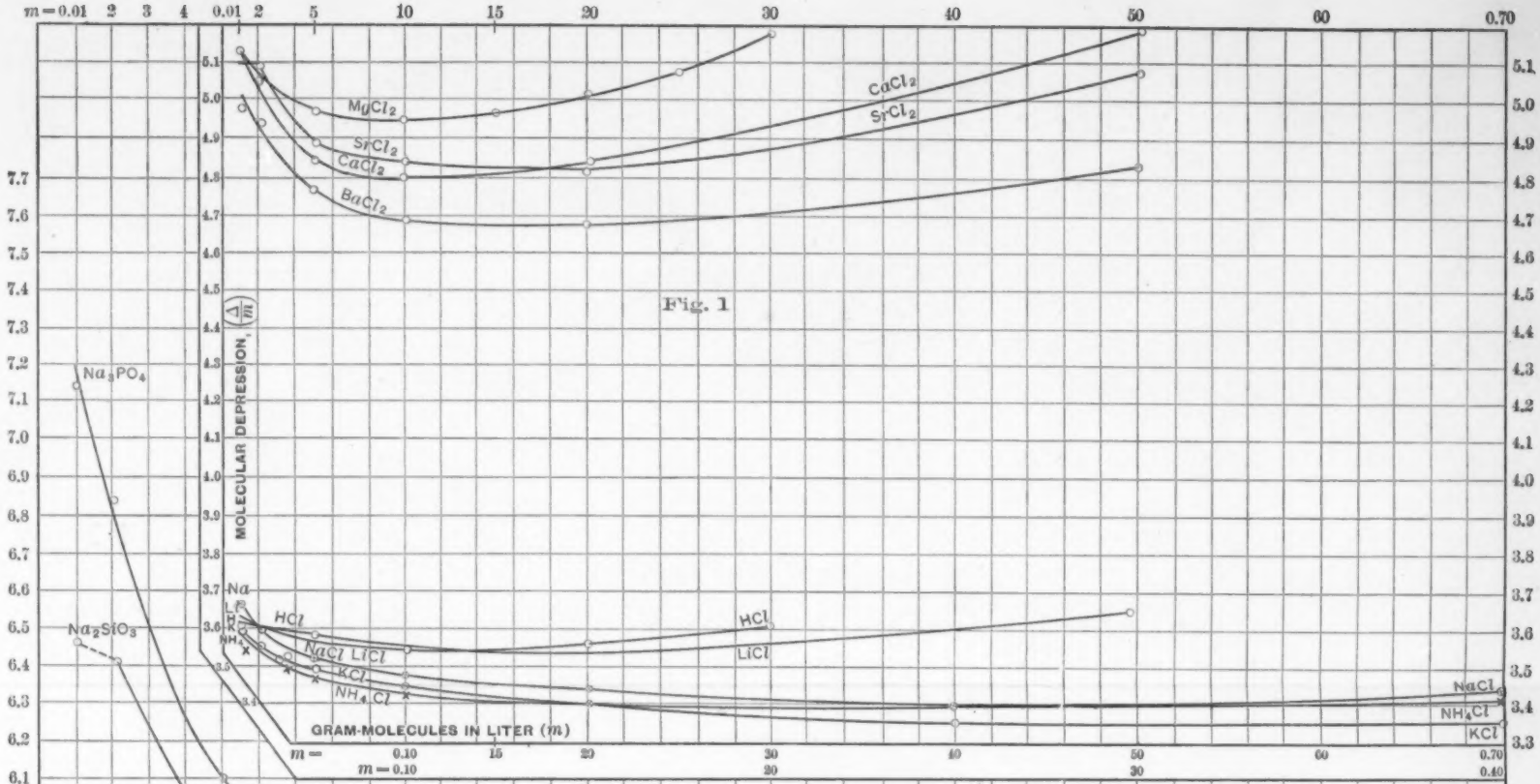

m = 0.01 2 3 4 0.01 2 5 10 15 20 30 40 50 60 0.70
MgCl2
SrCl2
CaCl2
BaCl2
MOLECULAR DEPRESSION, (Δ/m)
Na
Li
K
NH4
HCl
NaCl LiCl
KCl
NH4Cl
GRAM-MOLECULES IN LITER (m)
m = 0.10 15 20 30 40 50 60 0.70
m = 0.10 20 30 40 50 0.40

Fig. 1

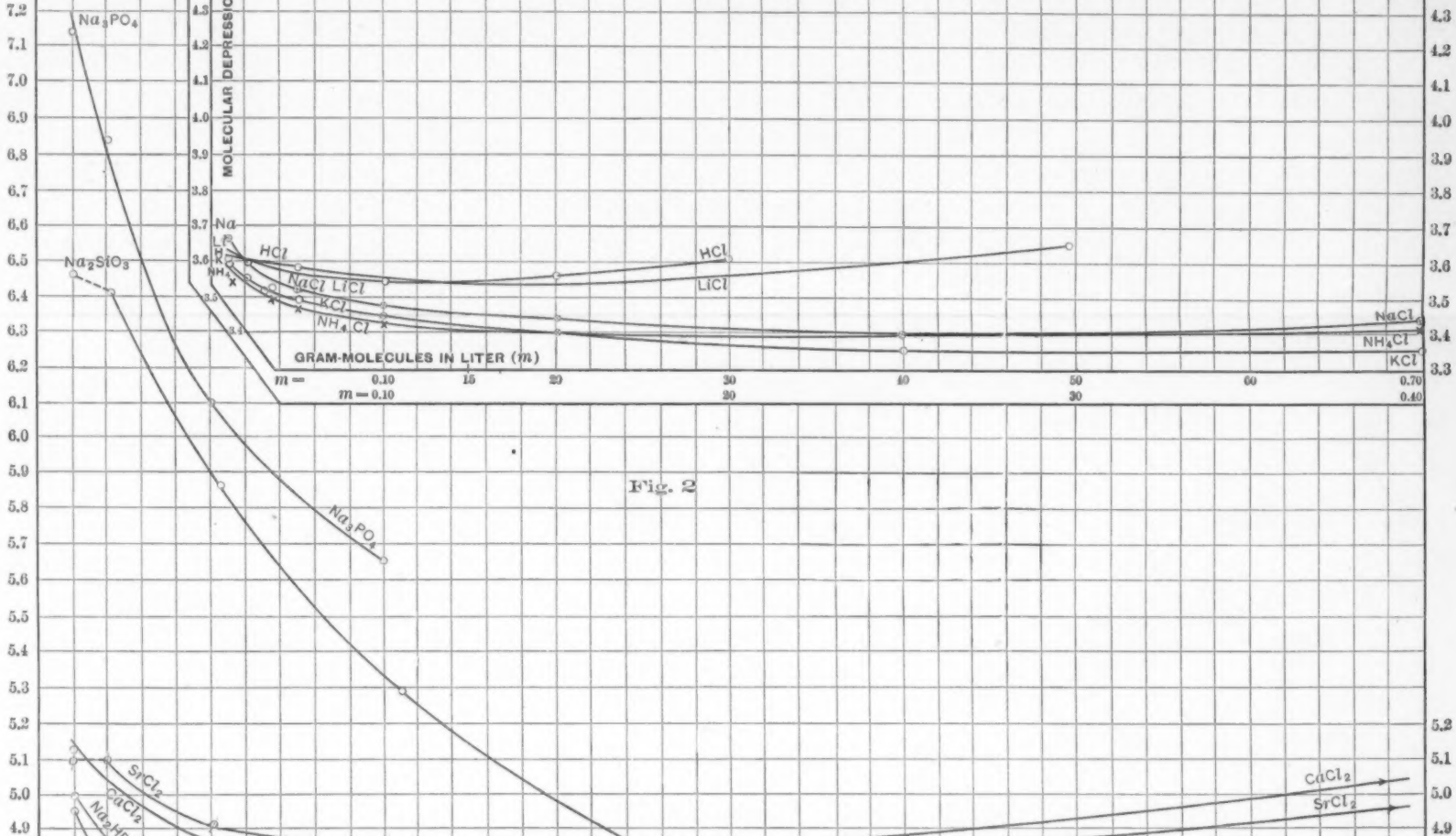

Na3PO4
Na2SiO3
Na3PO4
SrCl2
CaCl2
CaCl2
SrCl2

Fig. 2

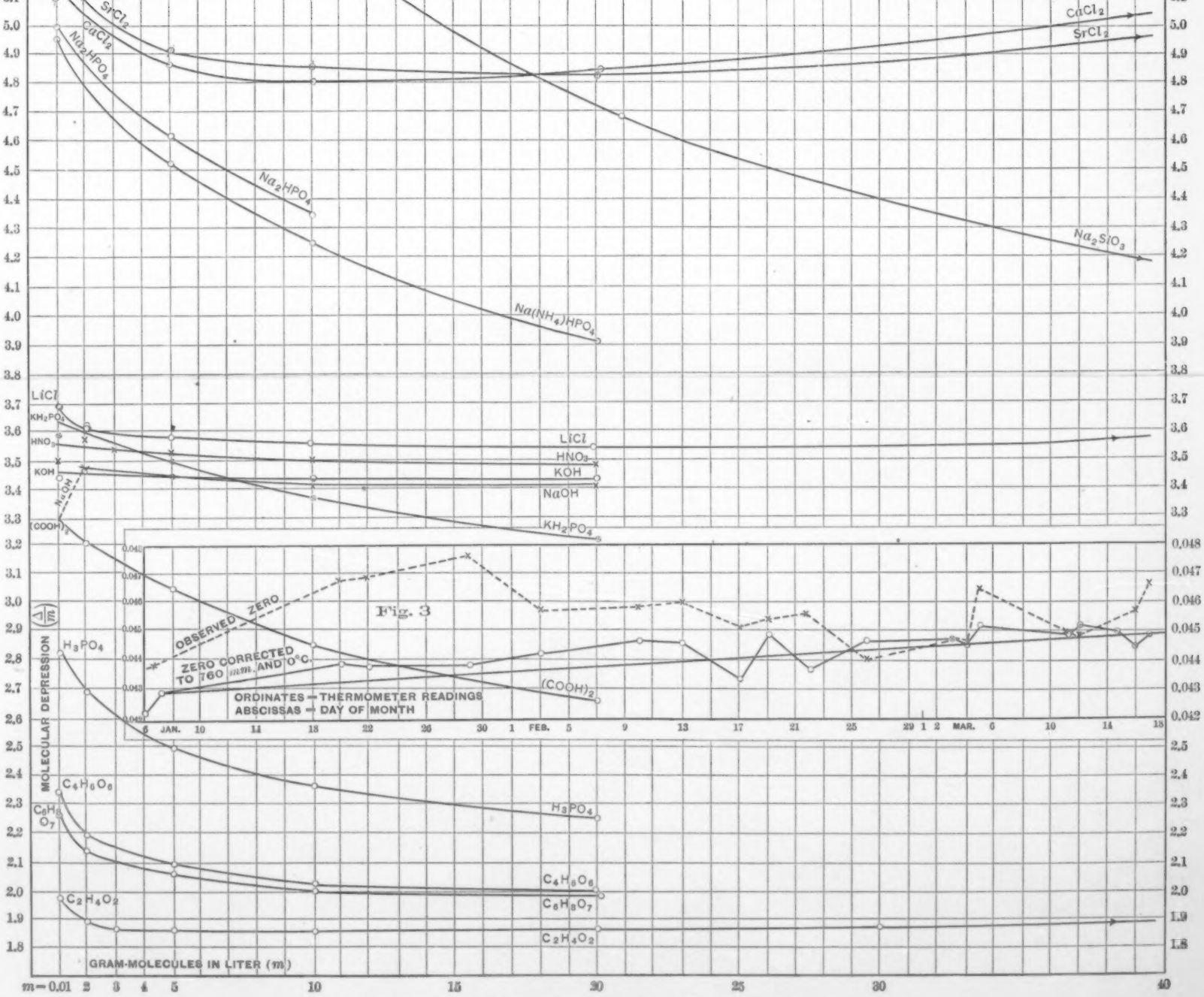

MOLECULAR DEPRESSION $\frac{\Delta}{m}$
GRAM-MOLECULES IN LITER (m)
m = 0.01 2 3 4 5 10 15 20 25 30 40
$CaCl_2$
$SrCl_2$
Na_2HPO_4
Na_2SiO_3
$Na(NH_4)HPO_4$
LiCl
KH_2PO_4
HNO_3
KOH
NaOH
$(COOH)_2$
H_3PO_4
$C_4H_6O_6$
$C_6H_8O_7$
$C_2H_4O_2$
OBSERVED ZERO
ZERO CORRECTED TO 760 mm. AND 0°C.
ORDINATES = THERMOMETER READINGS
ABSCISSAS = DAY OF MONTH
JAN. FEB. MAR.

Fig. 3

A METHOD FOR ENERGY MEASUREMENTS IN THE INFRA-RED SPECTRUM AND THE PROPERTIES OF THE ORDINARY RAY IN QUARTZ FOR WAVES OF GREAT WAVE LENGTH.[1]

By Ernest Fox Nichols.

IN previous determinations of the distribution of energy in the infra-red spectrum, either the principle of the thermoelement, or of the more modern bolometer, has been almost without exception the basis of measurement.[2]

In the present study, however, a modified form of the Crookes radiometer has proved so efficient that I take the liberty of describing briefly the apparatus and method by which the observations on quartz, given in the second half of the paper, were made.

I. Apparatus and Method.

1. *The Spectrometer.*

A diagram showing the relation of parts of the reflecting spectrometer used is given in Fig. 1. Rays enter the instrument through the bilateral slit s_1, are brought to parallelism by the concave mirror S_1, and, after reflection on the plane mirror S_2, traverse the prism P, are again collected by the concave mirror S_3, and brought to focus at s_2 in the tube F. The only unusual feature of the arrangement is the introduction of the plane mirror S_2 rigidly attached to the prism, a modification due to Wadsworth,[3] in which, contrary to the usual process, the telescope remains fixed, and the spectrum is made to travel across the field of view by rotating the combined prism and mirror. This adjustment is

[1] Read before the Berlin Academy, Nov. 5, 1896.

[2] Pringsheim [Wied. Ann., 18, p. 32 (1883)], in the study of certain wave lengths in the infra-red solar spectrum, used a Crookes torsion radiometer combined with a grating, but the form of apparatus differed, in many respects, from the arrangement here to be described.

[3] Phil. Mag., 38, p. 337, 1894.

necessary to the present method, because, unlike the bolometer, the radiometer is not conveniently portable.

The eye-piece in the tube F was removed, and a second bilateral slit s_2 was brought into the focal plane of the concave mirror S_3. Rays emerging from this slit were collected by the rock-salt lens

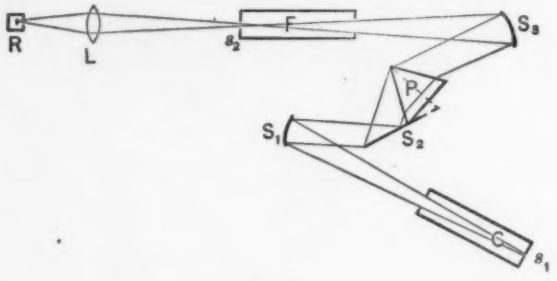


Fig. 1.

L, and brought to focus on one vane of the radiometer at R. The large fluorite prism P ($\phi = 60° 0'$) was calibrated in accordance with Paschen's [1] indices of refraction.

The calibration curve was tested in the visible spectrum, and found correct to 2 units in the fourth decimal place. In the infra-red the curve was again tested for the middle of the absorption band in sylvite, given at $\lambda = 7.08\,\mu$ by Rubens,[2] and here observed at $\lambda = 7.088\,\mu$ according to the curve. At this point a sylvite plate 4 mm. thick transmitted only 6 per cent of the incident energy. This may be accepted as evidence of the purity of the spectrum obtained, and of the absence in this region of more than a small percentage of stray rays of shorter wave lengths.

2. *The Radiometer—Construction.*

The details of construction of the radiometer will be doubtless most easily understood from Fig. 2, which shows a section of the instrument facing the spectrometer.

The figure is drawn to scale, and represents the instrument at half its natural size. The outer case A, a block of bronze with an axial boring from the top to within 5 mm. of the base, is supported upon three leveling screws, and is closed at the top by a bell of

[1] Wied. Ann., 53, p. 301, 1894. [2] Wied. Ann., 54, p. 481 (footnote), 1895.

glass *B* ground on the upper surface of the case. *H* is a stop-cock to cut off the connection to a Raps' mercury pump used to produce the vacuum. The case *A* contains two lateral borings: *C*, closed by a plate of mirror glass through which the deflections of the suspension are read, and *F*, closed by a fluorite plate through which the rays to be measured enter the radiometer. The arrangement of parts in the window *F* is seen in Fig. 2 *a*, which shows a sectional plane perpendicular to the former one.

The circular fluorite plate *P*, 5 mm. thick, is held in a screw fastening with rubber packing at *d*, and the whole mounted on a brass plate cemented to the case. In the boring *F* a short brass tube *r* is soldered, which extends to within 2 mm. of the axis of *A*, and carries a thin plate of mica *k* on its inner end.

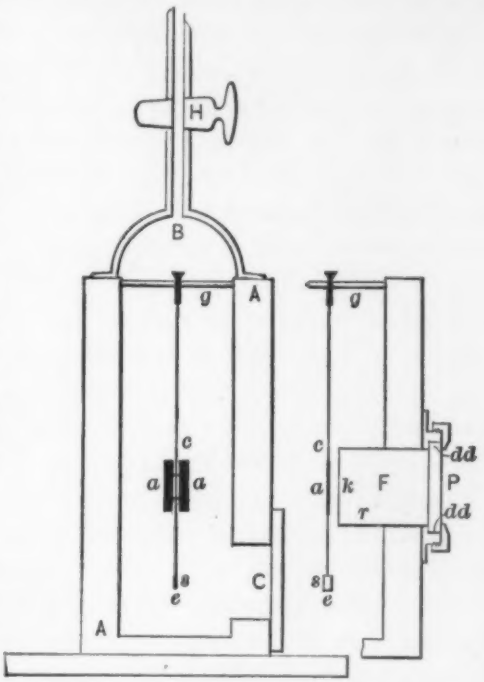


Fig. 2. Fig. 2*a*

Directly behind the mica plate hang the two equal mica vanes *aa*, both blackened on the same side, which form the important part of the torsion suspension. The vanes are held together by thin whips of drawn glass, and on the line midway between them is fastened the glass fiber *ce*, which forms the axis of rotation and carries near its lower end the mirror *s*. A very fine quartz fiber attached at *c* is suspended from the bridge *g*, and gives the directive force to the system.

The total weight of the suspension was 7 *mg*.

3. *The Radiometer as a Measuring Instrument.*

The sensitiveness of the radiometer was shown by Crookes[1] to be closely connected with the pressure of the gas in the inclosing vessel. A study at comparatively high pressures begun by Stoney and Moss[2] showed that the sensitiveness for the same pressure changed with the distance of the blackened vane from the opposite wall, increasing as the distance decreased.

Crookes[1] also observed that in the region of pressures where the radiometric sensitiveness was high, the logarithmic decrement of a torsion pendulum began to decrease rapidly with the pressure. These are the principal considerations that affect the present instrument, which, when the vanes were 2½ mm. from the mica plate and the pressure[3] in the vessel 0.05 mm., had a full period of vibration of twelve seconds, and was at its maximum sensitiveness. With further pumping the period of vibration could be brought down to eight seconds, but the shortening was accompanied by a decrease in sensitiveness. With greater pressure the period increased until it became aperiodic, and at atmospheric pressure if the upper end of the fiber was given 90° twist fully a minute elapsed before the suspension followed to its new position.

Near the maximum point the sensitiveness changes very slowly, so that the period of vibration is here the better test for the pressure sought.

If the vanes be brought within a millimeter of the mica window, for pressures greater than 0.1 mm., the sensitiveness is much increased, but the disadvantage is twofold, as the change involves an increased period, and the throws for small quantities of energy are greater in proportion than for large quantities.

For pressures near, or below, the maximum sensitiveness, small changes in the distance have no noticeable effect either on the sensitiveness or on the period.

Under the conditions which prevailed throughout the measurements the throws of the radiometer were proved proportional to the energy in several different ways; one of which was the meas-

[1] Proc. Roy. Soc., Nov. 16, 1876. [2] Proc. Roy. Soc., Feb. 22, 1877.

[3] Measured with the MacLeod gauge.

urement of the reflection percentage as dependent upon the wave length in the case of a fluorite surface under an incidence angle of 25°.[1]

The results obtained are compared in Table I. with reflection computed by the Fresnel formula, using Paschen's[2] observed indices of refraction. Wave lengths appear in the first column, observed reflections in the second, computed reflections in the third, and the differences in the fourth.

TABLE I.

REFLECTION OF FLUORITE.

$$r = 25°. \quad R = \frac{R_\perp + R_\parallel}{2}.$$

λ	*R* obs.	*R* comp.	Δ	λ	*R* obs.	*R* comp.	Δ
0.59	0.031	0.032	−1	4.0	0.030	0.030	0
1.00	0.031	0.032	−1	4.5	0.029	0.029	0
1.50	0.031	0.031	0	5.0	0.029	0.028	+1
2.00	0.031	0.031	0	5.5	0.029	0.028	+1
2.36	0.030	0.031	−1	6.0	0.028	0.027	+1
2.50	0.031	0.031	0	6.5	0.028	0.026	+2
3.00	0.031	0.031	0	7.0	0.027	0.025	+2
3.50	0.031	0.030	+1				

The sensitiveness at which the radiometer was held during the measurements which follow, was such that the rays from a candle at a distance of 6 m., when allowed to fall on one of the vanes, gave a deflection of 60 divisions on a millimeter scale at a distance of 1 m. from the instrument. This corresponds to a throw of more than 2100 scale divisions for a candle 1 m. away.

The compensating action of the two vanes was so nearly perfect, that rays from a source directly in front of the radiometer, which, when allowed to fall upon either vane alone gave a throw

[1] These observations were made by comparing the reflection of fluorite with that of silver as a standard, as in the case of quartz to be described later. As the reflection of fluorite is only about 3 per cent of the corresponding reflection of silver, throws — the larger of which was from thirty to forty times the smaller — were directly compared, and the test of proportionality was consequently a very severe one.

[2] Wied. Ann., 53, p. 301, 1894.

of 60 scale divisions, gave less than a millimeter when both were exposed. Thus it was possible to have an extremely sensitive instrument which at the same time held steadily to a fixed zero point, and gave throws trustworthy to the tenth of a millimeter.

As compared with the linear bolometer or the thermopile, the present form of radiometer has the following advantages: —

1. It is uninfluenced by all magnetic and thermo-electric disturbances, which render work with a very sensitive galvanometer tedious and unsatisfactory.

2. It can be more accurately compensated against rays which do not come from the source to be measured, and is consequently more free from "drift."

3. The radiometer is free from any disturbance corresponding to the air currents that arise about the warmed bolometer-wire.

It has, however, the following disadvantages: —

1. It is not as easily portable as either the bolometer or the thermopile.

2. All the rays to be measured must traverse the window of the radiometer, and be subject to its selective reflection and absorption.

3. In its present form the radiometer cannot be separated from a mercury air pump for more than a week at a time and remain sensitive.

II. OBSERVATIONS ON QUARTZ.

Our knowledge of the optical properties of quartz in the visible spectrum has been extended in the one direction by observations of Sarasin[1] in the ultra-violet, and in the other, by observations of Mouton,[2] and later of Rubens,[3] in the infra-red. Rubens' observations extend to a wave length $\lambda = 4.2\mu$. Beyond this point direct measurements of refractive indices are impossible because of the heavy absorption which in quartz begins in this region.

The present study begins here, and consists of observations of the reflection and transmission of quartz between the wave lengths

[1] Archiv. des Sc. Phys., 3, 10, p. 303, 1883. [2] Comptes Rend., 88, p. 1190, 1879.
[3] Wied. Ann., 53, p. 277, 1894, and 54, p. 480, 1895.

$\lambda = 4\mu$ and $\lambda = 9\mu$, where for another reason — the absorption of the fluorite prism used for dispersion — these observations come to an end.

1. *The Observation of Reflection.*

The reflection of quartz was not compared directly with the intensity of the incident beam, but for convenience with the reflection of silver, which had been previously determined.

The study of silver was made by comparing the beam reflected under an angle of 15° with the direct, by means of the "swinging arm" apparatus used earlier by Rubens.[1] The mirror studied was a silver deposit on glass.

The results are given in Table II., which contains also the values for the reflection percentages of silver observed by Rubens[1] and

TABLE II.

λ	Nichols.	Rubens.	Langley.	λ	Nichols.	Rubens.
0.35	—	—	61	0.90	96.0	95.8
0.38	—	—	73	1.00	—	96.5
0.40	—	—	79	1.15	—	97.0
0.43	82.7	—	—	1.40	—	97.4
0.44	86.4	—	—	1.65	—	97.7
0.45	—	87.0	85	2.00	97.2	97.3
0.49	90.1	—	—	2.50	96.5	97.0
0.50	—	88.3	89	3.00	97.3	98.3
0.54	91.5	—	—	3.50	98.3	—
0.55	—	90.3	91	4.00	100.0	—
0.59	91.6	—	—	6.00	99.8	—
0.60	—	92.7	92	7.00	99.6	—
0.64	93.6	—	—	8.00	99.0	—
0.65	—	93.3	93	8.40	99.5	—
0.70	—	94.5	93	8.65	99.2	—
0.75	95.0	—	94	9.00	100.0	—
0.80	—	95.2	—	—	—	—

by Langley.[2] The agreement is seen to be very close. That the values here given are however slightly higher, in the visible spectrum, than those of either Rubens or Langley, can doubtless be

[1] Wied. Ann., 37, p. 249, 1889. [2] Phil. Mag., 27, p. 10, 1889.

explained by differences in polish, upon which the reflection in this region in great measure depends.

In the infra-red, on the contrary, the reflection is but little affected by ordinary differences in polish, and a silver mirror grown perceptibly yellow with age gave the same percentage of reflection at wave lengths 6μ and 8μ as a perfectly fresh one. For waves longer than 4μ observations show the reflection to be so nearly total, that in the comparison with quartz the intensity of the beam from the silver mirror was taken as unity.

A prism surface cut perpendicular to the optic axis of a negatively rotating quartz crystal was chosen for the study of the reflection of quartz.

To gain the very small incidence angle of 5°, the arrangement of apparatus shown in Fig. 3 was adopted, in which p is the zircon plate of the Linnemann burner which supplies the energy. L_1 is a rock-salt condensing lens, M_1 the device for holding the mirrors to be compared, and M_2 a silver plane mirror to direct the rays into the spectrometer slit s_1. A shutter was introduced at S and a diaphragm at D. The two plates forming the sides of the spectrometer slit were covered with squared paper, and the position of the real image formed by the lens L_1 of a platinum point at c served as a check to control the adjustment in the change from silver to quartz and the reverse.

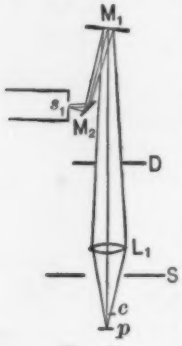


Fig. 3.

The surfaces to be compared were carefully mounted in two exactly equal carriers, each of which fitted into the holder M_1, and were held firmly in place by two springs.

To show the treatment of single observations and at the same time the behavior of the radiometer, the observations at wave lengths $8.72\,\mu$ and $8.52\,\mu$ are given entire. Of the fifteen series of observations, made at as many different wave lengths between $8\,\mu$ and $9\,\mu$, the former furnishes the best agreement of single values among themselves, and the latter the worst.

Table III.

TWO SETS OF OBSERVATIONS OF THE REFLECTION OF QUARTZ *Q* COMPARED WITH THE REFLECTION OF SILVER *S*.

u^2, the percentage of reflection, is obtained alternately from $\frac{2\,Q_n}{S_n + S_{n+1}}$ and $\frac{Q_n + Q_{n+1}}{2\,S_{n+1}}$.

$\lambda = 8.72\,\mu$. Slits 1.5 mm. wide.			$\lambda = 8.52\,\mu$. Slits 1 mm. wide.		
Scale readings.	Throws.	u^2	Scale readings.	Throws.	u^2
S_1 532.2 / 497.1	35.1	—	S_1 532.9 / 506.1	26.8	—
Q_1 531.8 / 509.9	21.9	62.7	Q_1 533.0 / 514.2	18.8	71.9
S_2 531.9 / 497.0	34.9	62.9	S_2 532.7 / 507.0	25.7	72.0
Q_2 531.9 / 510.0	21.9	62.9	Q_2 532.9 / 514.6	18.3	70.9
S_3 531.8 / 496.9	34.9	62.5	S_3 533.1 / 507.0	26.1	70.9
Q_3 531.7 / 510.0	21.7	62.5	Q_3 532.6 / 513.9	18.7	72.9
S_4 531.8 / 497.0	34.8	62.2	S_4 532.3 / 506.9	25.4	74.0
Q_4 531.4 / 509.9	21.5	62.3	Q_4 532.7 / 513.7	19.0	74.0
S_5 531.3 / 497.1	34.2	—	S_5 532.1 / 506.3	25.8	—
Average, 62.6 per cent.			Average, 72.4 per cent.		

All the observed values of the reflection percentages of quartz are collected together in the second column of Table IV., the respective wave lengths being given in column 1. Column 3 gives the wave-length interval, $\lambda_1 - \lambda_2$ in μ, corresponding to the angular width of the slits used, both of which were always opened equally wide. These values thus show in a sense the purity of the spectrum at each of the observed points.

TABLE IV.

λ	n^2 $i=5°$	$\lambda_1-\lambda_2$	T obs.	$\lambda_1-\lambda_2$	T_1 corr.	κ_0^2 10^{-6}
4.20	—	—	90.0	0.07	—	—
4.40	—	—	89.7	0.07	—	—
4.50	3.40	0.07	92.0	0.07	99.0	0
			93.6	0.10		
4.70	—	—	90.1	0.06	—	—
4.80	—	—	89.3	0.07	—	—
4.90	—	—	85.9	0.07	—	—
5.00	3.00	0.07	69.7	0.07	75.0	41
			71.3	0.10		
5.05	—	—	71.0	0.05	—	—
5.10	—	—	74.6	0.05	—	—
5.15	—	—	74.5	0.05	—	—
5.20	—	—	71.1	0.07	—	—
5.25	—	—	62.3	0.05	—	—
5.30	2.73	0.07	54.1	0.05	57.0	174
5.40	—	—	67.8	0.06	—	—
5.50	—	—	72.2	0.10	—	—
5.70	—	—	80.0	0.11	—	—
5.80	2.50	0.09	81.1	0.05	85.4	16
5.90	—	—	75.5	0.11	—	—
6.00	—	—	72.8	0.11	—	—
6.10	—	—	70.6	0.11	—	—
6.20	—	—	60.2	0.11	—	—
6.25	1.80	0.11	59.2	0.11	61.9	174
			59.4	0.05		
6.30	—	—	63.3	0.10	—	—
6.35	—	—	68.1	0.11	—	—
6.40	—	—	77.2	0.11	—	—
			75.9	0.11		
6.45	1.46	0.10	79.8	0.11	83.5	42
			82.3	0.05		
6.50	—	—	77.2	0.10	—	—
6.55	—	—	72.0	0.10	—	—
6.60	—	—	68.1	0.10	—	—
6.65	—	—	68.1	0.05	—	—
6.70	1.19	0.10	67.6	0.10	69.0	121
6.80	—	—	74.5	0.10	—	—
6.90	—	—	80.5	0.10	—	—
7.00	0.65	0.12	81.3	0.09	82.2	23
7.10	0.46	0.12	[1] 79.3	0.09	80.1	62
7.20	0.44	0.12	75.3 [2]	0.09	76.2	76
7.30	0.31	0.12	70.4	0.09	71.2	121
7.40	0.29	0.12	66.7	0.09	67.4	166

[1] Graphically interpolated.

[2] Double dispersion applied to transmission spectrum in this region.

TABLE IV. (*continued*).

λ	μ^2 $i=5°$	$\lambda_1-\lambda_2$	T obs.	$\lambda_1-\lambda_2$	T_1 corr.	κ_0^2 10^{-6}
7.50	0.42	0.12	59.5	0.09	60.1	286
7.60	0.86	0.09	51.5	0.09	52.5	466
7.70	1.34	0.09	35.8	0.09	36.9	1,149
7.80	3.25	0.09	18.0	0.09	19.3	3,215
7.90	[1]6.00	0.09	12.2 [2]	0.09	13.9	4,747
7.92	6.69	0.09	—	—	—	—
8.00	14.0	0.08	5.6	0.09	7.8	8,136
8.02	17.2	0.08	—	—	—	—
8.05	[1]23.0	0.08	3.1	0.09	5.8	10,240
8.10	—	—	>0.5	0.09	—	—
8.12	43.3	0.08	—	—	—	—
8.22	63.3	0.08	—	—	—	—
8.32	70.4	0.08	—	—	—	—
8.42	75.0	0.08	—	—	—	—
8.52	72.4	0.08	—	—	—	—
8.62	51.1	0.08	—	—	—	—
8.65	56.5	0.08	—	—	—	—
8.67	58.4	0.08	—	—	—	—
8.72	62.6	0.12	—	—	—	—
8.80	67.1	0.12	—	—	—	—
8.82	64.0	0.12	—	—	—	—
8.90	60.5	0.08	—	—	—	—
8.92	58.0	0.11	—	—	—	—
9.00	51.5	0.08	—	—	—	—
9.02	49.2	0.11	—	—	—	—

Wave lengths and reflection percentages are shown again in a curve in the plate opposite page 312. The curve falls very gradually from $\lambda = 4.5\ \mu$ to a minimum at $7.4\ \mu$, where the observed reflection was only 0.29 per cent.

From $\lambda = 7.4\ \mu$ to $\lambda = 8.45\ \mu$ the curve rises with surprising rapidity, reaching a maximum value of 75 per cent near the latter wave length, after which it falls to a second minimum of 51 per cent near $\lambda = 8.6\ \mu$ and rises to a second maximum of 66 per cent at $\lambda = 8.8\ \mu$. It then falls regularly to $\lambda = 9\ \mu$, where the observations of reflection end.

The error in the reflection percentages here given is due wholly

[1] Graphically interpolated.

[2] Double dispersion applied to transmission spectrum in this region.

to the presence of a small percentage of rays of shorter wave length, never entirely absent from measurements in this region, and which here has the effect to bring the two maximum points too low, and the second one lower in proportion than the first. The first minimum at $\lambda = 7.4\,\mu$ is probably too high, as will be seen later.

2. *The Observation of Transmission.*

For the study of transmission, the lens L_1 (see Fig. 3) and the lamp were brought into line with the collimator of the spectrometer, and the intensity of the direct ray compared with that of the ray transmitted through a thin plate of quartz placed directly before the slit.

The plate used was a thin scale cut perpendicular to the optic axis of the crystal and mounted in a glass frame with a free aperture 10×5 mm. The spectrum of light reflected from the plate under an angle of 15° gave 10 + interference bands between the Fraunhofer lines *C* and *D*, from which the thickness 18 μ was computed.

Column 4 of Table IV. gives the observed percentages of transmission T for the wave lengths given in column 1. Column 5 contains the wave-length interval $\lambda_1 - \lambda_2$ corresponding to the angular width of the slits; and column 6 gives the values of T_1, *i.e.* the values of T corrected for the reflection at both surfaces, computed by the formula

$$T_1 = \frac{T}{(1 - 2\,u^2)^2}$$

The observed transmissions extend from $\lambda = 4.2\,\mu$ to $\lambda = 8.05\,\mu$ and the observations are plotted as a curve in the plate with wave lengths as abscissæ and percentages of transmission as ordinates.

Beyond $\lambda = 7\,\mu$, to make sure of the purity of the spectrum, which later became important, a second fluorite prism and slit were introduced into the path of the rays before they entered the spectrometer, thus giving double dispersion. In the path of the curve between 4.2 μ and 7 μ are five maxima and four minima, of which three in each case are sharply defined. From 7 μ on,

the curve sinks so rapidly that it was impossible to follow it beyond 8.1 μ, where, through a thickness only two and one-fourth times the wave length of the incident ray, only a doubtful 0.5 per cent struggled through.

Although the whole region between 8.1 μ and 9 μ was carefully searched, no trace of transmitted energy large enough to measure was discovered.

TABLE V.

λ	ν − Root.	ν + Root.	u^2 corrected.	ν accepted.	ν Rubens.	Δ
4.50	0.692	1.450	—	1.450	1.442	+ 8
5.00	0.706	1.417	—	1.417	1.411	+ 6
5.30	0.719	1.393	—	1.393	1.386	+ 7
5.80	0.730	1.368	—	1.368	1.343	+ 25
6.25	0.765	1.309	—	1.309	1.287	+ 22
6.45	0.785	1.274	—	1.274	1.257	+ 17
6.70	0.803	1.242	—	1.242	1.212	+ 30
7.00	0.853	1.172	—	1.167[1]	1.145	+ 22
7.10	0.873	1.144	—	1.125[1]	1.117	+ 8
7.20	0.877	1.141	0.150	1.080	1.089	− 9
7.30	0.899	1.113	0.025	1.032	1.056	− 24
7.40	0.899	1.112	0.000	1.000	1.020	− 20
7.50	0.880	1.137	0.135	0.930	0.979	− 49
7.60	0.835	1.199	0.568	0.861	0.933	− 72
7.70	0.798	1.256	—	0.798	0.881	− 83
7.80	0.702	1.432	—	0.702	0.819	− 117
7.90	0.611	1.645	—	0.611	0.746	− 135
8.00	0.478	2.172	—	0.478	0.657	− 179
8.05	0.366	—	—	0.366	0.603	− 237

3. *The Dispersion.*

In general, it is possible to compute ν, the index of refraction, for every wave length λ for which u^2 and D_1 are known, by substituting, in the Cauchy formula, the observed values of u^2 and the extinction coefficient κ_1. In reflection at normal incidence, the intensity of the ray $u_{\parallel}^2$ polarized in the plane of incidence and the ray $u_{\perp}^2$ polarized in the plane at right angles are equal, and for 5°, the observed incidence, the equality may, within the limits of error, still be assumed.

[1] Interpolated graphically.

The simpler expression, that for $u_{\parallel}^2$, was consequently used in the computation, and the observed reflection, u^2, put into the formula

$$u^2 = \frac{(\cos i - \sqrt{\nu^2 - \sin^2 i})^2 + \kappa_1^2}{(\cos i + \sqrt{\nu^2 - \sin^2 i})^2 + \kappa_1^2}, \quad (1)$$

which may be expressed as an explicit function of ν of the form

$$\nu^2 = \sqrt{\sin^2 i + \left\{\cos i \left(\frac{1+u^2}{1-u^2}\right) \pm \sqrt{\cos^2 i \left(\frac{1+u^2}{1-u^2}\right)^2 - (\kappa_1^2 + \cos^2 i)}\right\}^2}, \quad (2)$$

in which the extinction coefficient κ_1 for the incident angle i may, in this case, be put equal to κ_0, the extinction coefficient for normal incidence. These values, computed from the formula [2]

$$T_1 = e^{\frac{-4\pi d\kappa_1}{\lambda}}, \quad (3)$$

are given in column 6, Table IV. In the formula, $d = 18\,\mu$, the thickness of the plate, and λ is the given wave length.

As the value of κ_0^2 at $8.05\,\mu$, the highest observed, is only 102×10^{-4}, $\kappa_0^2 m$ (2) was put equal to zero, so that the refraction, in this case, depends solely upon the reflection, and the modified Fresnel formula is applicable within the limits of error.

Equation (2) gives two values of ν for every value of u^2, depending on which root of the inner radical is chosen. The index given by the positive root corresponds to a reflection u^2 for a ray striking at an angle of 5° from the rarer into the denser medium, while the negative root gives an index which would give the same reflection for the same incident angle for a ray crossing the boundary in the opposite direction. Both values are given in Table V., and again as curves in the plate. From the beginning out to $\lambda = 7.4\,\mu$, where u^2 reaches its lowest value, there is no question which index is the correct one, but beyond this point the choice is a doubtful one, as will be seen later. The equation as a whole possesses one important peculiarity: whenever u^2 is very small, minute changes in u^2 produce comparatively large changes in ν. At $7.4\,\mu$, for

[1] Wüllner Lehrbuch d. Physik, Bd. II., p. 536, Leipzig, 1883.
[2] Wüllner Lehrbuch d. Physik, Bd. II., pp. 123–126.

example, $u^2 = 0.29$ per cent, and $\nu = 1.11$ or 0.9; while for $u^2 = 0$, $\nu = 1$.

Reflection percentages in the neighborhood of zero must therefore be very carefully treated, and the possibility of false values due to stray light, never entirely absent in such work, must be taken into account.

The wide slits which it was necessary to use, and the nearness in the reflection spectrum to a maximum point of at least two hundred and fifty times the intensity here involved, make the conditions for stray energy most favorable. The importance of using double dispersion, which furnishes the best precaution against such an error, was unfortunately first realized after the measurements had all been taken. The observed reflection percentages in this region are in consequence doubtless too large.

If the reflection of 0.29 per cent observed at $7.4\,\mu$ was due wholly to stray energy from near $8\,\mu$, which is not unlikely under the circumstances, and the reflection percentages from $7.2\,\mu$ to $7.6\,\mu$ be corrected by this amount, and ν again computed for the corrected values, points are obtained which are connected by broken lines on the plate.

The position of these broken lines is suggested by the whole course of the curves outside this doubtful region, and the writer regards these new values of ν as nearer correct than the old ones, in which case the most natural conclusion is that the curves intersect rather than touch at $7.4\,\mu$. Quartz and air are thus believed to change places here, and later, air to play the part of the denser medium; but it is impossible, on the basis of these results alone, to say with certainty which of the two possible dispersion curves is the correct one.

The course of either curve between $7\,\mu$ and $8\,\mu$, together with the heavy absorption and the change in reflection, which at $\lambda = 7.4\,\mu$ is probably less than that of any body known in the visible spectrum, and which at $\lambda = 8.4\,\mu$ rivals that of burnished silver for violet light, show conclusively that quartz in this region passes over completely from a non-metallic to a metallic body.

4. *The Ketteler-Helmholtz Dispersion Formula.*

Rubens,[1] supplementing his own careful observations with the other experimental material in hand at that time, computed for quartz the five constants in a form of the Ketteler-Helmholtz dispersion formula, which is rigorously applicable only where the absorption bands are two in number, and linear. The values of ν given by these constants appear in column 6 of Table V. and again in the plate.

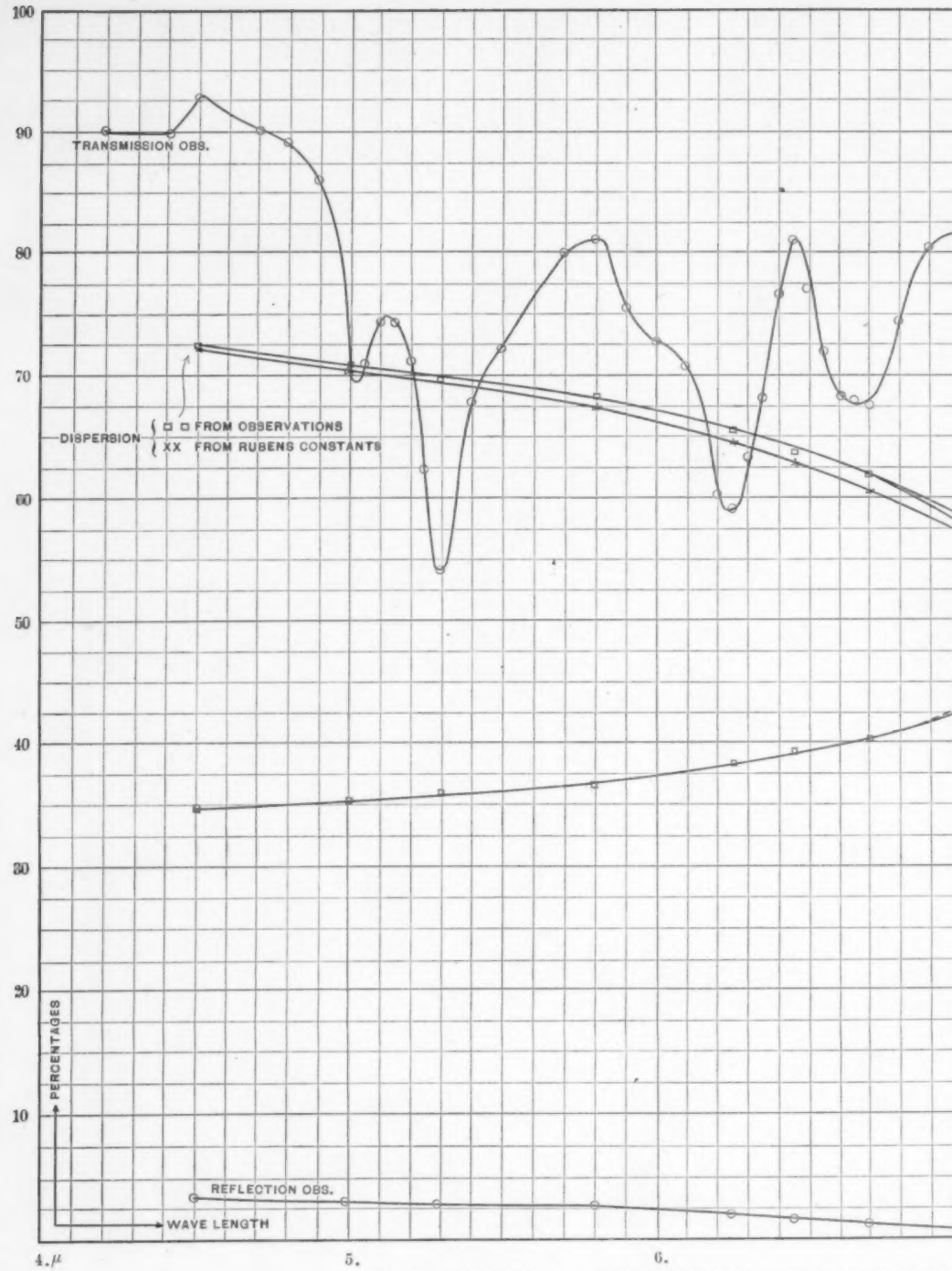
Only the general character of the curve thus obtained and that of the preferred curve computed from the observations can be considered the same. Before $\lambda = 7.2\,\mu$ the latter curve lies higher, afterward lower than the former one.

While the indirect method here employed for measuring the refractive index is at best a very rough one, still the divergence of the two curves is systematic, and is so great that the discrepancy cannot be entirely accounted for by the inaccuracies of the method. For the same wave length the difference between the refractive indices given by the two curves finally reaches 39 per cent. On the other hand the wave-length difference given by the two curves for the same index of refraction nowhere exceeds $0.16\,\mu$ and the agreement is closer than might have been expected when it is considered that the furthest point observed by Rubens was at $\lambda = 4.2\,\mu$. On the basis of constants computed for the region lying before this wave length, which were introduced into a special form of the general equation, the curve has been continued a full octave farther to $\lambda = 8.05\,\mu$.

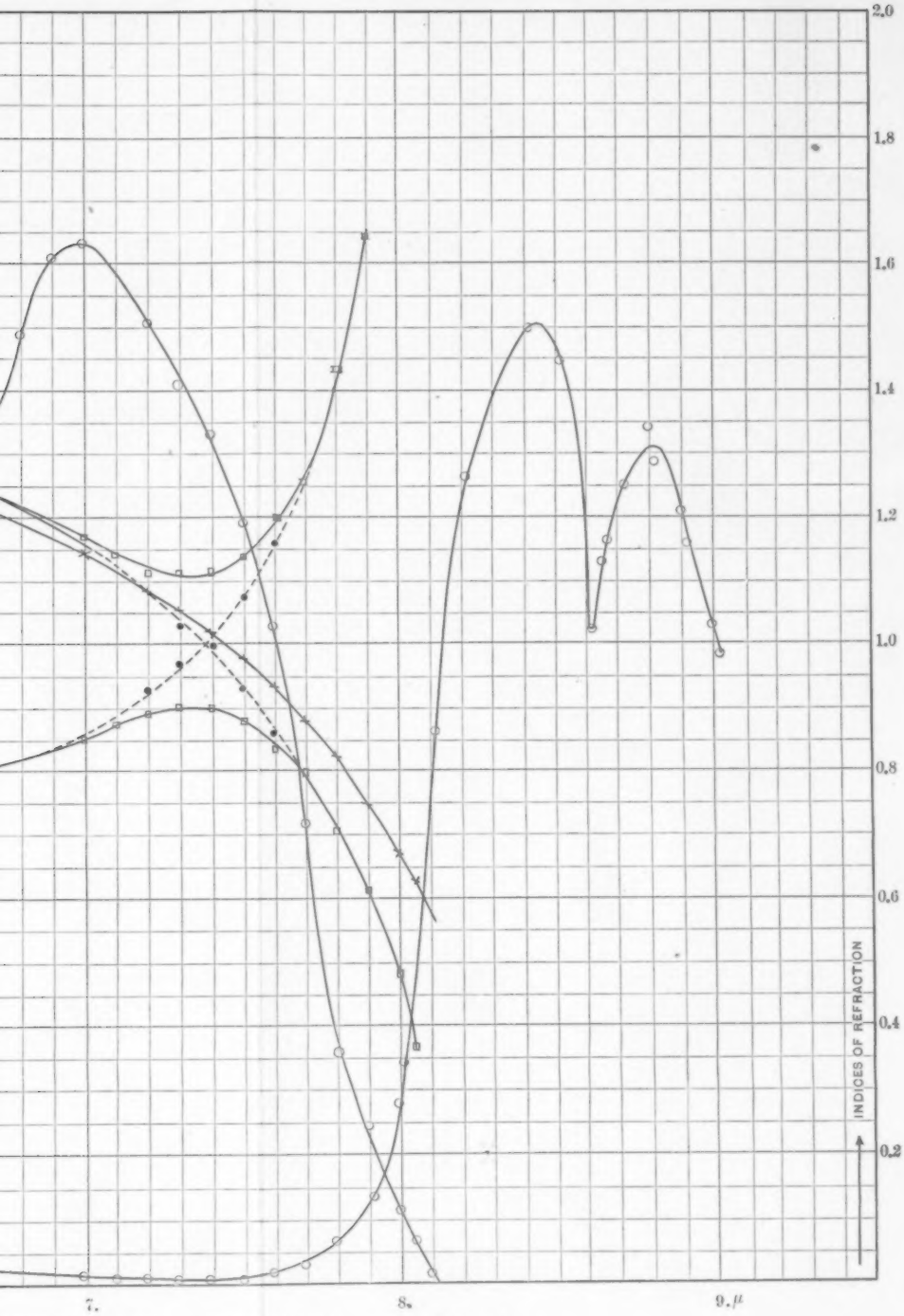
It is also possible that there are still other absorption bands beyond $\lambda = 9\,\mu$, not taken into account in the formula, which influence the dispersion in the region studied.

Before closing I wish to thank Professor E. Warburg for the friendly interest he has taken in these experiments, and for the means to further them put at my disposal. I wish to express, also, my deep appreciation of the kindly interest in this study shown by Professor Heinrich Rubens, under whose direction it was made, and to acknowledge my indebtedness to him for many helpful

[1] Wied. Ann., 53, p. 277, 1894, and 54, p. 480, 1895.



E. F. NICHOLS: REFLECTION, TRANSMISSION



ISSION, AND DISPERSION OF QUARTZ.

suggestions. I am further indebted to the kindness of Professor E. Pringsheim, at whose suggestion the work of building the radiometer was undertaken, for friendly advice concerning many details in the construction.

PHYSICAL INSTITUTE OF THE UNIVERSITY OF BERLIN,
June 1895–June 1896.

HEAT RAYS OF GREAT WAVE LENGTH.

BY HEINRICH RUBENS AND E. F. NICHOLS.

SINCE we have become accustomed to think of waves of electrical energy and light waves as forming component parts of a common spectrum, the attempt has often been made to extend our knowledge over the wide region which has separated the two phenomena, and to bring them closer together, either by cutting down the wave length of electrical oscillations — which, through the remarkable experiments of Righi[1] and later of Lebedew,[2] have been reduced to $\frac{1}{100}$ of the shortest waves measured by Hertz — or by the discovery and measurement of longer heat waves. In this direction no noticeable progress has been made since Langley's well-known experiments in 1886. On the contrary, since the determination of the dispersion of rock salt by Paschen[3] and one of the present writers,[4] it has been necessary to modify Langley's[5] estimate very considerably, so that the longest heat waves previously observed can scarcely have exceeded 0.015 mm., or about twenty-five times the wave length of sodium light. The farthest limit of exact measurement reached by Paschen,[6] in his determination of the dispersion of fluorite, was at 0.00943 mm., or approximately sixteen times the wave length of sodium light. The great difficulty which accompanies the study of infra-red waves of great wave length is that these rays form only the minutest part of the total energy emitted by the flame or incandescent body used as a source. Consequently, if their properties are to be studied, these waves must be separated from others which completely overlap and conceal them.

[1] A. Righi, Rendiconti Acc. d. Lincei (5), 2, 505 (1893).
[2] P. N. Lebedew, Wied. Ann., 56, 1 (1895).
[3] F. Paschen, Wied. Ann., 53, 337 (1894).
[4] H. Rubens, Wied. Ann., 54, 476 (1895).
[5] S. P. Langley, Ann. de Chim. et de Phys. (6), 9, 433 (1886).
[6] F. Paschen, Wied. Ann., 53, 301 (1894).

To accomplish this end a prism of either rock salt or fluorite has commonly served.

The heat spectrum formed by a fluorite prism, because of absorption, contains no waves which exceed 0.01 mm. in length, while that from a rock-salt prism contains these waves and still longer ones in measurable quantity. That the diathermacy of this substance is by no means without limit, was conclusively shown by Gustav Magnus[1] twenty-six years ago, when he discovered that a rock-salt plate 5 mm. thick transmitted only about one-third of the energy emitted by a rock-salt crystal heated to a temperature of 150°.

The loss of energy due to the selective absorption of a prism is indeed avoided in the grating, but this escape is cumbered with disadvantages even more formidable; for not only are the diffraction spectra very weak in energy, but they overlap in such a way that it is almost impossible to separate them.

The new dispersion theories, however, suggest a method, by the use of which, unassisted by either prism or grating, homogeneous rays of great wave length may be obtained, and in sufficient quantity to make the determination of their properties and wave length possible. Helmholtz' dispersion theory, based on the laws of electromagnetic resonance, and that of Ketteler, based on the theory of elasticity, both lead to the same final equation which was shown in an earlier study by one of the present writers[2] to be in close agreement with the observed facts. In a region of the spectrum where there is little or no absorption, the formula common to both hypotheses is

$$n^2 = b^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2},$$

in which n is the index of refraction corresponding to the wave length λ, and λ_1, λ_2, are wave lengths approximately in the middle of the two neighboring absorption bands, one in the ultra-violet and the other in the infra-red. b^2, M_1, and M_2 are other constants characteristic of the substance.

Theoretically, the absorption in the region of these two bands

[1] G. Magnus, Pogg. Ann., 139, 445 (1870).

[2] H. Rubens, Wied. Ann., 53, 267 (1894), and Wied. Ann., 54, 476 (1895).

near λ_1 and λ_2 is very heavy, approaching the absorption of a metal for light rays; for a weaker absorption could not influence the dispersion. As absorption in this degree is necessarily accompanied by a metallic reflection, the wave lengths corresponding to the absorption band in any substance would appear magnified out of all due proportion in the spectrum of rays reflected from it. Suppose, for example, that within the region covered by the absorption band the reflection be twenty to thirty times as great as in other parts of the spectrum; as was shown by one of the present writers[1] to be the case in the reflection of quartz near wave length 0.0085 mm.; then in the spectrum of rays after three reflections from the substance, these waves would lose comparatively little in intensity, while the intensity of waves lying on either side would be brought down in the ratio of $(20)^3$ or $(30)^3$ to 1; *i.e.* as 8000 or 27000 to 1. If, further, a source of energy be chosen which emits these waves advantageously[2]—as will necessarily be the case if the body heated is of the same substance as the reflectors—the spectrum after three reflections will contain, in measurable quantity, only the wave lengths sought.

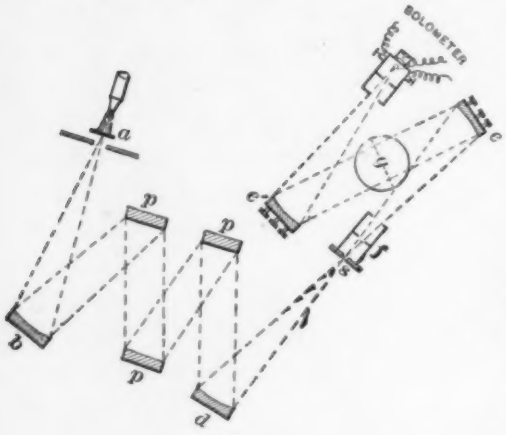


Fig. 1.

From the foregoing considerations the arrangement of apparatus shown in Fig. 1 will be easily understood. In the figure *a*,

[1] E. F. Nichols, PHYSICAL REVIEW, Vol. IV. p. 297; Berichte d. Berl. Acad., Nov. 5, 1896.

[2] From "advantageously" it is not to be inferred that the greater part of the rays emitted by the source chosen shall correspond to the wave length of the absorption band, but rather that the emission of these rays in proportion to others shall be greater than from an ideal black body heated to the same temperature. In the case of glowing fluorite powder, for example, the wave lengths emitted which correspond to that region of absorption showing metallic reflection form only the smallest portion of the total energy. Still the ratio is larger than would be gained by using another powder in its place.

the source of energy, was a bit of platinum foil 15 × 15 mm., coated with the substance to be studied, and heated from behind by a blast lamp. A concave silver mirror at *b* reflected a bundle of parallel rays, which afterward underwent three successive reflections from the surface *p* of the substance in question. By means of the second concave silver mirror at *d*, the rays were brought to focus on the slit of a reflecting spectrometer. A transmission grating made of wires $\frac{1}{6}$ mm. thick could be placed at will on the spectrometer table at *g*, in the path of the rays, for the purpose of wave-length determination. To obtain a sufficiently sensitive bolometer, it was necessary to work with a galvanometer of the highest efficiency. As such the "Panzer Galvanometer," recently designed by Dr. du Bois and one of the present writers, gave most satisfactory results, and kept a very constant zero point, so that in spite of the magnetic disturbances occasioned by the Berlin street traffic, it was possible to recognize with certainty temperature differences of 0°.00001 of the exposed bolometer. The slit width chosen for experiments — equal to that of the bolometer — was 3.6 mm., which corresponded to an angular width of 0° 20′ on the spectrometer circle. The bolometer first tried consisted of thirteen strips of iron 0.25 mm. wide by 0.005 mm. thick, which, because of its large resistance and high temperature coefficient, had proved very sensitive in previous work. This instrument was replaced later by a platinum bolometer; for it was discovered that the layer of lampblack with which it was coated did not absorb more than about 5 per cent of the rays obtained from fluorite. The new instrument — supplied us through the kindness of President Kohlrausch — consisted of five strips of platinum $\frac{1}{2}$ mm. wide by 0.001 mm. thick, and was constructed in accordance with the design of Lummer and Kurlbaum.[1] The absorbing layer was in this case a coating of platinum black, deposited electrolytically. This instrument, although less sensitive for waves of shorter wave length, gave deflections twice as large as the earlier one for the long rays resulting from three reflections on fluorite. It thus appears that platinum black possesses an absorption covering a much wider region than lampblack, which fact has been shown

[1] O. Lummer and F. Kurlbaum, Wied. Ann., 46, 204 (1892).

in a different way by the experiments of Lummer and Kurlbaum.

By the foregoing method, the two substances quartz and fluorite have already been studied. For both of these substances the constants in the Ketteler-Helmholz equation had been computed from direct observations of refractive indices, pushed as far into the infra-red as the absorption in each case permitted. From Paschen's[1] computation for fluorite, the middle of the infra-red

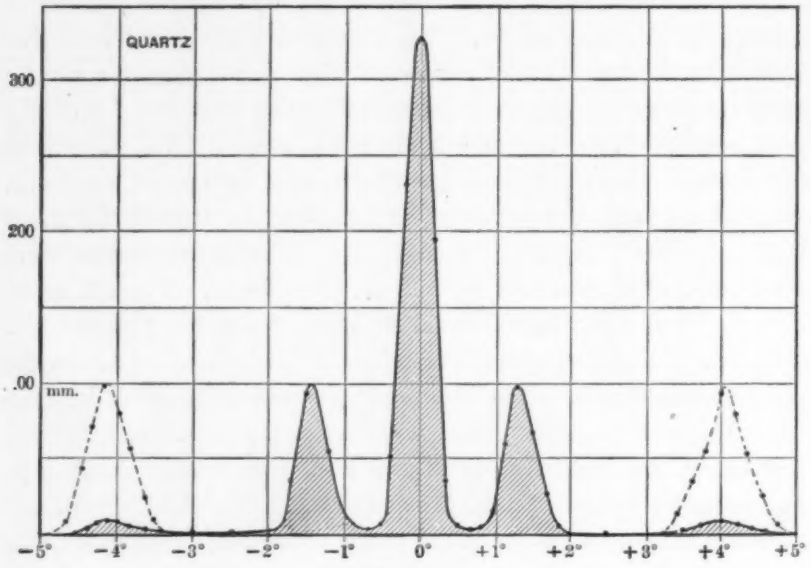


Fig. 2.

absorption band was predicted at wave length 0.03 mm. Similar computation, by one of the present writers,[2] placed the band in quartz at wave length 0.01 mm. The peculiar relation of these constants to the remaining quantities which enter into the equation renders the correct placing of such a band somewhat uncertain; for, although its existence influences the dispersion in the observed region markedly, its exact position plays a comparatively minor rôle. From the theory, therefore, after three reflections from quartz, or from fluorite, only rays in the neighborhood of either 0.01 mm. or 0.03 mm. wave length should remain, and the

[1] F. Paschen, Wied. Ann., 53, 812 (1894). [2] H. Rubens, *l.c.*

experiments have proved, in the main, the correctness of the reasoning.

In Figs. 2 and 3, two series of observations, one on fluorite and the other on quartz, are shown graphically. The ordinates give the galvanometer deflections, and the abscissæ the corresponding readings of the circle of the spectrometer, which characterize the position of the bolometer in the spectrum.[1] In both figures, the central image stands out plainly, and symmetrically on either hand the diffraction images of the first order. In the case of quartz, the images of the third order are also easily recognized.[2] The grating constant, which was unusually large, was optically determined by the position of the diffraction images of the sodium line out to the image of the twenty-third order, which gave a constant 0.37165 mm. Measured on the dividing engine, the constant was 0.37167 mm.; 1° deviation, therefore, indicated a wave length of 0.0065 mm. approximately.

Experiment with Quartz.

The three reflecting surfaces in this case were from two prisms and a plate, all cut perpendicular to the optic axis of the crystal. The deviation of the maximum point of the diffraction image of the first order from the middle of the central image was 1° 22′, and that of the third order 4° 6′. The mean wave length of the observed rays thus computed gave in the one case 0.00887 mm., in the other 0.00882 mm. The agreement between the two values lies wholly within the probable error, and furnishes, at the same time, a valuable check upon the accuracy of the grating to a deviation of 4°.

In consequence of the wide slit and the equally wide bolometer used, it is impossible to draw conclusions concerning the distribution of energy in the diffraction image itself; but the fact that

[1] In Fig. 3, which gives graphically the series of observations made with fluorite, the scale of ordinates chosen is ten times as great as that in Fig. 2, which shows a similar series with quartz.

[2] In order to show more plainly the position of the maxima in the spectra of the third order, the ordinates corresponding to the galvanometer deflections were multiplied by ten, which gave rise to the dotted-line curves. Because of the peculiar construction of the grating, the spectra of the 2d, 4th, 6th, ... orders are wanting.

the image of the third order appears little or no wider than that of the first, shows that the rays must be fairly homogeneous, and can scarcely comprise a wave-length difference greater than 10 per cent. Using a bit of platinum foil coated with iron oxide at a temperature of about 1000° as a source, it was easy with the arrangement of apparatus described to effect a heating of the bolometer of 0°.02, which corresponded to a deflection of about 2 m. The properties of rays of equal wave length have long been known, as it is possible to obtain them in measurable intensity in the spectrum of a rock-salt, or even fluorite, prism.

Experiment with Fluorite.

The rays emitted by an incandescent platinum foil coated with fluorite powder after three reflections from fluorite retain scarcely more than 0.001 of their initial energy.

This remnant, when undispersed, was capable of raising the bolometer temperature about $\frac{1}{800}°$ (120 mm. deflection), and the greatest patience and care were necessary, with this small quantity of energy, to establish the exact position of the maxima in the images of the first order lying on either side of the center.

In Fig. 3, which represents one of the several series of observations for this purpose, it is seen that the maximum energy in the diffraction spectrum of the first order lies 3° 45′ from the middle of the central image, which corresponds to a wave length of 0.0244 mm. The mean wave length resulting from other series varied from 0.024 mm. to 0.025 mm.

Heat rays of $\frac{1}{40}$ mm. wave length show in many respects quite different properties from those previously studied, which lie much nearer the visible spectrum. They are, for example, completely absorbed by a fluorite plate 2 mm. thick. A rock-salt plate 5 mm. thick lets through only about 3 per cent and an equally thick silvite plate about 5 per cent. In fact, after considerable searching we have not yet succeeded in finding a substance as diathermous for these rays as fluorite is for infra-red rays to a wave length of 0.007 mm.

The least absorbent substance so far discovered is vitreous

chloride of silver in the form of thin plates, which Schultze-Sellack,[1] in the year 1870, showed to be more and more diathermous the greater the wave length of the incident rays. A plate of chloride of silver 0.5 mm. transmitted about 70 per cent of the incident rays, while a plate $2\frac{1}{2}$ mm. thick absorbed 75 per cent of the remaining energy.

To study the optical behavior of lampblack in this region, a plate of chloride of silver, the absorption of which had been earlier

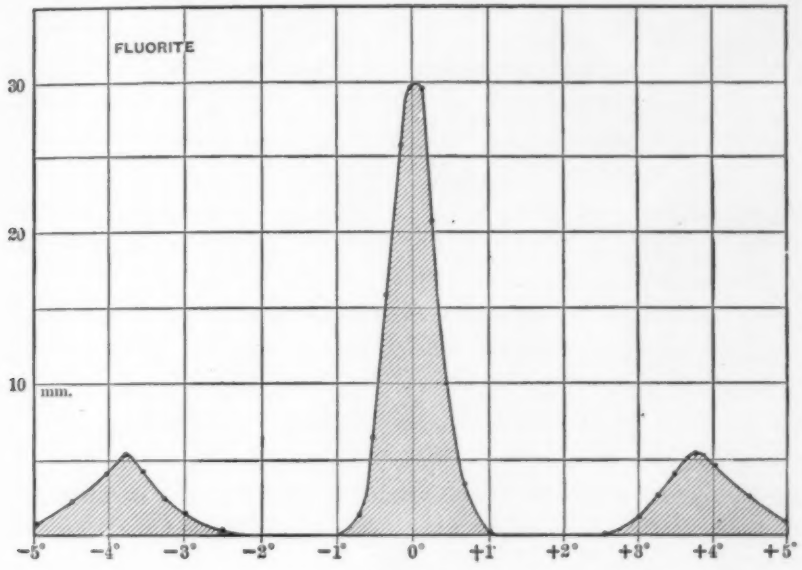


Fig. 3.

determined, was blackened in the smoke of a candle until it was completely opaque to the sun's rays, and the absorption again measured, with the surprising result that the increase did not exceed 5 per cent, which shows that lampblack cannot be considered a black body for these rays.

It appeared, further, of interest to find out whether these waves were destructively absorbed by water vapor and carbon dioxide gas, as is the case with shorter heat waves. To this purpose a blast of carbon dioxide gas and dry air were alternately blown into the collimator (Fig. 1, *f*) of the spectrometer, but no corresponding

[1] C. Schultze-Sellack, Pogg. Ann., 139, 182 (1870).

changes were perceived in the intensity of the rays. The same experiment was tried with water vapor with like result. If either absorb in this region the action must be very weak.

If the numbers obtained from the foregoing experiments for the mean wave length of the rays resulting from three reflections on quartz, and on fluorite, be compared with the values computed from the Ketteler-Helmholtz dispersion formula for the middle of the absorption bands in each case, the observed value for quartz is 10 per cent less than the computed, and for fluorite 20 per cent. This may perhaps be accounted for by the inaccuracies unavoidable in the computed values, but there may be errors affecting the experimental values as well. For example, nothing is so far known of the relation between the absorption of the platinum black, with which the bolometer was coated, and the wave length. In case the absorption decreases as the wave length increases, which is by no means unlikely, the same quantities of energy would give rise to smaller and smaller deflections of the galvanometer as the wave length increased. This would obviously cause a displacement of the true maximum toward shorter wave lengths. Further, the curve which represents the distribution of energy of a black body when heated first rises as the wave length increases, reaches a maximum, and then sinks asymptotic to zero. The maximum of the energy curve of the source used lies certainly at a wave length much shorter than those here considered; consequently within the absorption band the longer waves are again at a disadvantage compared with the shorter ones.

In any case, one is justified in regarding the agreement between the observed and computed wave lengths as close enough to confirm the utility of the theories involved.

In addition to the experiments with quartz and fluorite, similar trials were made with rock salt and sylvite, which, according to the course of their dispersions in the region where it has been studied, should, after multiple reflection, give rays very considerably longer than those here recorded; but we have not yet succeeded in getting sufficiently faultless surfaces of these substances to make the experiments successful. We still hope, however, to overcome these difficulties, and to refine the present method until we are in posi-

tion to study waves of much greater wave length ; and, further, to obtain a much higher degree of sensitiveness by substituting the improved radiometer[1] for the present bolometer.

Before closing, it will be of interest to call attention to the fact that, in respect to wave lengths, the rays corresponding to the infra-red absorption band in fluorite lie almost exactly midway between the shortest ultra-violet rays observed by Schumann[2] ($\lambda = 0.0001$ mm.) and the 6 mm. electrical waves of Lebedew, when the interval is reckoned according to octaves, as is customary in acoustics. On the other hand, if the spectrum be laid out according to uniformly increasing wave lengths, the space between the longest heat waves and the shortest electrical waves is 240 times greater than the length of the whole ultra-violet, visible, and infra-red spectrum taken together, and if reckoned according to the uniformly increasing number of oscillations is 250 times smaller than the combined ultra-violet, visible, and infra-red spectrum.

BERLIN: PHYSICAL INSTITUTE OF THE UNIVERSITY.

[1] E. F. Nichols, *l.c.*

[2] V. Schumann, Wiener Acad. Ber., 102, 415, and 625 (1893).

MINOR CONTRIBUTIONS.

ON THE FORMATION OF LEAD SULPHATE IN ALTERNATING CURRENT ELECTROLYSIS WITH LEAD ELECTRODES.

BY SAMUEL SHELDON AND MARCUS B. WATERMAN.

IN a paper on the Capacity of Electrolytic Condensers[1] it was shown that condensers formed by submerging the ends of platinum wires in dilute sulphuric acid were of very large capacity. These were, however, not adapted to commercial ends, because the capacity was not constant with varying voltages, and especially because the efficiency was very low. Efforts to determine whether electrolytic condensers, formed with lead electrodes, might not have a much higher efficiency, acting much in the same manner as the lead plates of a storage battery, yielded the results imparted in this paper.

Condensers were made with electrodes of lead wire, 0.5 mm. in diameter, passing through glass tubes and imbedded, at the ends, in a cement formed of venice turpentine and shellac. Only the polished ends of the wires were in contact with the electrolyte (dilute H_2SO_4). Endeavors to determine the capacity of these condensers, by the method of reversals outlined in the above-mentioned paper, yielded nothing but non-concordant results. The cause of these discrepancies was suggested upon introducing the condensers into an alternating current circuit in a vain endeavor to determine whether the phase was shifted by their introduction. The immediate result, upon passing the current, was the dissolution of the electrodes and the formation of insoluble lead sulphate. The latter, after a long time, settling to the bottom of the electrolytic cell.

The results of an investigation concerning the causes which influence the dissolution of lead electrodes in H_2SO_4, when traversed by alternating currents, are given in the tables which follow.

There are three main causes which affect the quantity of lead dissolved per coulomb of electricity passing through the circuit. They are the current density at the electrodes, the frequency of the alternations of the current, and the temperature of the electrolyte.

[1] PHYSICAL REVIEW, Vol. II., No. 12.

The Influence of Current Density.

Three pairs of electrodes, made of hollow cylinders of polished lead of about 0.8 cm. diameter, were submerged in a 5 per cent solution of H_2SO_4 to such a depth that the individual electrodes of the pairs exposed areas of 4, 8, and 12 square centimeters respectively to the action of the electrolyte. The interiors of the cylinders were filled with a cement not affected by the acid. Current from a small Westinghouse alternator was sent through these cells connected in series, and its magnitude was measured by an electrodynamometer. The time during which the circuit was closed was determined by means of a stop watch. Each pair of electrodes was weighed before and after each run. It was desirable that the run should be moderately long in order that the loss in weight of the electrodes might be determined with sufficient accuracy. On the other hand, it was difficult to maintain the temperature of the electrodes constant during a long run, owing to the heat generated by the current. The durations of the runs in each case were so chosen as to yield the best results. In calculating the number of coulombs which had passed through the cell in a given time, the assumption has been made that the shape of the current curve given by the alternator was sinusoidal. This assumption does not involve a very large error, as was proved by comparison of the curve, yielded by the alternator and obtained by the wiping contact method, with a sine curve of equal maximum value. The machine gave four complete alternations per revolution. The maximum positive and negative values of the current were, in arbitrary units, $+93$, -86.5, $+86$, -91, $+91.5$, -93, $+93$, -93. Plotting a curve of current i as a function of the time t, the area $\int idt$, inclosed between this curve and the time axis, represents the quantity of electricity passed through the circuit. During one revolution these areas, as determined by a planimeter and expressed in arbitrary units, were $+211$, -205, $+202$, -214, $+214$, -217, $+220$, -210. The area contained between a sine curve and the same portion of the time axis intercepted by the current curve, the maximum ordinate of the sine curve being 90.9, *i.e.* an average of the maximum current values, was 213. This is practically the same as the average of the current areas. It thus appears that no very great error is introduced, if the coulombs passing through the circuit in t seconds be taken as the product of the $\sqrt{\text{mean}^2}$ current, as obtained from the electrodynamometer, and $\frac{2t}{0.707\pi}$. The results given in Table I. are graphically represented by Fig. 1.

TABLE I.

Temperature.	Weight of lead dissolved. Milligrams.	Duration of run. Seconds.	Surface of electrode. Sq. centimeters.	$\sqrt{\text{mean}^2}$ current. Amperes.	$\int idt$. Coulombs.	At 18° milligrams of lead dissolved per coulomb.	Current density. Amp. per cm.^{2}
16.98	33.3	600	12.0	0.452	271.0	0.124	0.0380
18.00	15.6	180	12.0	0.543	97.6	0.160	0.0452
21.30	26.8	180	12.0	0.723	130.0	0.214	0.0600
18.00	27.2	180	6.5	0.543	97.6	0.279	0.0835
21.37	37.7	180	8.0	0.723	130.0	0.302	0.0900
17.00	47.6	120	12.0	1.127	135.2	0.348	0.0940
17.17	104.6	600	4.0	0.452	271.0	0.382	0.1130
22.37	96.3	118	12.0	1.710	202.0	0.503	0.1420
17.30	75.5	120	6.5	1.127	135.2	0.553	0.1730
20.84	94.9	120	8.0	1.422	171.0	0.575	0.1780
20.97	126.1	300	4.0	0.755	226.0	0.579	0.1890
22.50	123.7	118	8.0	1.710	202.0	0.646	0.2140
20.65	122.2	180	4.0	1.020	183.7	0.690	0.2550
20.17	133.0	120	4.0	1.422	171.0	0.799	0.3560
23.49	157.8	118	4.0	1.710	202.0	0.834	0.4280
17.24	206.4	60	4.0	3.810	228.6	0.895	0.9520
16.77	220.0	60	4.0	4.037	242.2	0.895	1.0100

The Influence of Frequency.

In investigating the influence of the frequency of alternations upon the quantity of lead dissolved per coulomb, two methods of altering the frequency were employed. By the first, the speed of the motor which drove the alternator was varied so as to give from 13 to 145 complete alternations per second. At the lower speeds the electromotive force of the generator was small. Accordingly, to obtain a uniform current density throughout the range of frequencies, a small current was employed. For alternations between 0 and 20 per second a direct current was employed, and its direction was commutated by a slow speed revolving commutator of two sections, which was driven by a small motor. The current was measured by a Weston ammeter. At these low frequencies the rate of formation of the lead sulphate is very sensitive to small changes in the frequency, and there seems to be an unstable chemical condition. For instance, during one run with three alternations per second, after about thirty seconds the electrodes took on the dark brown color of a storage battery positive, and after that no sulphate appeared to be formed. With

two alternations per second the attack on the electrodes ceased after twenty seconds. At these low frequencies, therefore, the runs were of necessity of very short duration, and the loss in weight of the electrodes was very small. No great amount of accuracy can be claimed for the results. They are, however, interesting as indicating, in a general way, the relation which exists between the rate of loss and the frequency. As it was impossible

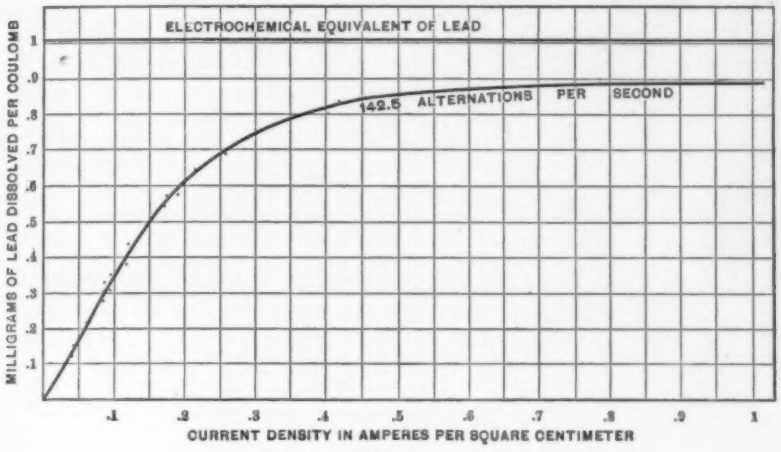


Fig. 1.

to obtain exactly the same current density in the various observations, the differences must be allowed for, if the different observations are to be connected. No great error will be introduced by assuming that the milligrams of lead dissolved per coulomb are directly proportioned to the current densities.

The results obtained are given in Table II., and are graphically represented in Fig. 2.

TABLE II.

Milligrams of lead dissolved per coulomb at 18°.	Number of alternations per second.	Current density in amperes per cm.^{2}	Milligrams of lead dissolved per coulomb at current density = 0.22.
0.202	2.0	0.209	0.212
0.334	3.0	0.221	0.333
0.523	4.0	0.222	0.520
0.618	5.0	0.220	0.618
0.714	5.5	0.223	0.705
0.756	10.1	0.226	0.735
0.800	20.1	0.226	0.779
0.785	84.2	0.246	0.703
0.646	142.5	0.224	0.635

The Influence of Temperature.

In determining the effect of temperature upon the amount of lead dissolved per coulomb of electricity, the commutated direct current was employed. The speed of the commutator was regulated to give such a number of alternations per second that small variations in frequency would have but little influence on the weight of lead dissolved per coulomb. A pair of electrodes, each exposing four square centimeters of surface to the action of the electrolyte, was placed in a beaker of 5 per cent H_2SO_4 at any desired temperature. Current at an electrode density of 0.215 amperes per square centimeter was passed through the cell for thirty seconds. The temperature during this interval remained practically constant. Maintaining, in this manner, the current density constant, the milligrams of lead dissolved per coulomb of electricity passed through the circuit was found to be 0.794, 0.744, and 0.683 for temperatures 17.134, 22.330, and 28.125° C., respectively. These results yield a temperature coefficient of

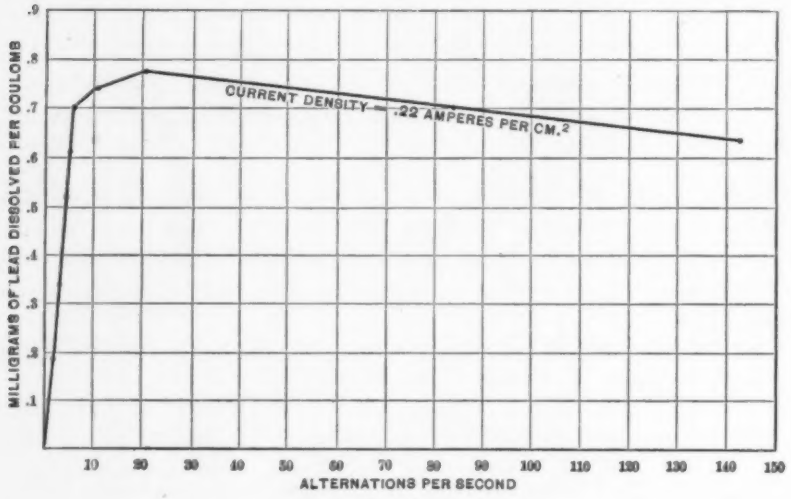


Fig. 2.

-0.0125; *i.e.* the current density remaining constant, the milligrams of lead dissolved per coulomb of electricity passed decreases 1.25 per cent of the amount dissolved at 18° C. for each degree rise of temperature above 18°.

Conclusion.

The authors have no theory to offer as explanatory of their results. The facts brought out are unquestionably associated, in some manner, with the

velocities or rates at which the involved chemical processes take place. The experiments on very low frequencies have developed the fact that PbO_2 is not soluble in H_2SO_4, or acted upon by the products of the electrolytic decomposition of H_2SO_4. The fact that $PbSO_4$ is formed with the alternating currents would seem to indicate that a lower oxide than the peroxide was first formed in quantity, and that this was afterwards acted upon by the electrolyte to form $PbSO_4$. If this be so, the velocity of formation of the lower oxide must be greater than the velocity of oxidation to PbO_2.

POLYTECHNIC INSTITUTE OF BROOKLYN, June, 1896.

POLARIZATION AND INTERNAL RESISTANCE OF A GALVANIC CELL.

BY B. E. MOORE AND H. V. CARPENTER.

THE electromotive force of many cells decreases very rapidly upon closed circuit, and after a period of rest it nearly recovers its original value. In some cells this is so marked that they are called "open circuit" cells. This is rather a conventional use. It means only that the cells cannot be used on closed circuit any considerable length of time. Carhart, in his *Primary Batteries*, gives curves for change in electromotive force, current, and internal resistance of a great many such cells. The cells are run for a certain period, and then allowed to recover for the same length of time. The total electromotive force, E, and fall of potential, E', over a known external resistance, R, are measured. The current can be calculated from the equation $C = \frac{E'}{R}$, and the internal resistance, r, is determined from the equation $r = \frac{E - E'}{E'} \cdot R$.

While this method reveals the fact and magnitude of polarization, it by no means localizes it. That is, it does not tell us how much polarization occurs at each electrode. In cells of the Leclancé type it has generally been assumed that the polarization occurs at the carbon electrode, and that the potential difference between zinc and solution is constant. The fall in electromotive force on closed circuit, at first rapid, has generally been attributed to the formation of gas liberated from the positive ion at the carbon electrode. The later decrease would therefore be slower, owing to the slow absorption of gas at the carbon. Depolarizers are therefore frequently added to minimize the formation of gaseous products. On the other hand, when the cell is thrown on open circuit, it was reasoned that the gas actually in contact with the electrode would be rapidly given off,

and thus occasion a rapid rise in electromotive force. However, the gas somewhat removed from the electrode surface would hinder the electromotive force from regaining its original value for some time. The following short experiment was carried out with the view of substantiating or of refuting this explanation.

A diamond carbon cell was taken. This is essentially a Leclancé cell with no depolarizer. Reliance is had upon the soft carbons to absorb the gas and communicate it ultimately to the air. The carbon electrode consisted of seven pencils, each 9 mm. in diameter, arranged in a circle 75 mm. in external diameter. The zinc electrode, 6 mm. in diameter, is located symmetrically as to the carbons. For the purpose of this experiment the zinc electrode was displaced 4.5 mm. from the center, and diametrically opposite it at the same distance from the center was placed a special carbon electrode of exactly the same electrode surface. The end of this carbon protruding from the solution was copper plated, and a wire was soldered to it for making connections. A fresh solution of chemically pure ammonium chloride, containing five ounces to the quart, constituted the electrolyte.

The object of the experiment was to measure the electromotive force and its changes upon closed and open circuit between the zinc and main carbons, to get the electromotive force between the zinc and special carbon at intervals, and also to obtain the electromotive force of the carbon series during the progress of the experiment. Such a procedure would evidently enable one to determine the amount of polarization at the electrodes of the main circuit, provided the tension of the special carbon remained constant. Taking off appreciable currents through the special carbon as a circuit is manifestly excluded. It became necessary, therefore, to use a condenser. Even the charging of the microfarad condenser at first disturbed the potential differences, and no carbon could be found which would show a zero electromotive force between the main carbons and special carbon. At last a strip of glass 2 mm. thick and 18 mm. wide was inserted between the zinc and special carbon, whose surface was only 3 mm. from the former at the nearest point. Repeated charging and discharging of the condenser now showed no change in the potential differences in different parts of the circuit. The special carbon ultimately used was taken from another similar cell and turned down to proper size. Its electromotive force in respect to the main carbons was -0.261 volts.

Figure 1 shows the arrangement of the connections. The zinc and special carbons are designated by a and b, respectively. The keys K_1, K_2, K_3, and K_4 are turned over by a pendulum swinging from left to right.[1] The time required for the pendulum to pass from K_1 to K_4 was about

[1] Carhart, PHYSICAL REVIEW, Vol. II., p. 392.

0.1 second. Keys *c*, *d*, and *e* make contact at the upper points unless depressed. By setting keys K_2 and K_3 only, and releasing the pendulum from its detent, we obtain the electromotive force of the main circuit, if *c*, *d*, and *e* are not disturbed. Had *c* been depressed, it would have given us the potential between the carbon electrodes, or had *e* instead of *c* been depressed, we should have obtained the total electromotive force of the zinc and special carbon circuit. It is evident that when keys K_1, K_2, K_3, K_4 are set, and keys *c* and *d* are depressed, we can measure the fall of potential over R_1. Under these conditions the special carbons and main carbons compose the battery. We can also measure the fall of potential over R, when either of the other two circuits is closed, by setting K_1, K_2, K_3, and K_4. R and R_1 were resistances of 1 ohm and 10 ohms respectively.

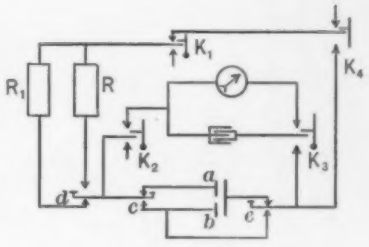


Fig. 1.

At the outset, repeated observations were taken upon the various circuits closed through the resistance R and R_1 for the above short-time period, 0.1 of a second. The ballistic galvanometer gave constant deflections in every case. Had there been a change of 0.5 mm. in the deflection, it could have been detected. To make a run upon the battery, the key K_1 was left in contact with the upper point, and key K_4 was set. In getting the total electromotive force of any circuit, it now becomes necessary to drop the detent to K_4 just before the liberated pendulum reaches key K_2. Key K_4 must promptly be set again. With a little practice the time required for this operation need not exceed two seconds. In measuring the fall of potential over R and R_1, open circuit was entirely avoided by stopping the pendulum with the hand before reaching key K_4. Depressing the keys *c* and *d* or *e* also opens the circuit, but the time is here also small, as they need only be depressed while the pendulum is making one swing from left to right. This only required one-half second. The time the battery was upon open circuit, during the run of thirty minutes, was therefore very small. Upon recovery key K_4 was set only when terminal potential was to be determined. Key K_1 was then also set, and the battery would therefore only be closed for 0.1 of a second.

In the table of results E, E_s, and E_c represent total electromotive forces upon the main circuit, the zinc and special carbon circuit, and the main carbon and special carbon circuit, respectively. E', E_s', and E_c' represent the corresponding terminal potentials. The latter is measured over R_1, which it became necessary to use in order to obtain appreciable readings

for E_e'. We will designate the internal resistances of circuits giving E, E_s, and E_e by r, r_s, and r_e, respectively. The resistance, r, began at 0.12 ohms and ended at 0.09. The resistance, r_s, began at 1.27 ohms, reached the value

TABLE I.

POLARIZATION.

Standard Clarke gave a deflection on the galvanometer = 80 = 1.434 volts.

Time.	E	E'	E_e	E_e'	E_s	E_s'
min. sec.						
0 00	1.368	1.020	−0.261	−0.144	1.614	0.738
0 15	—	1.017	—	—	—	—
1 00	1.260	—	—	—	—	—
1 45	—	1.013	—	—	—	—
2 45	—	1.011	—	—	—	—
3 30	—	—	0.395	—	—	—
4 15	1.206	—	—	—	—	—
5 30	—	1.010	—	—	—	—
6 30	—	—	—	0.045	—	—
7 30	1.161	—	—	—	—	—
8 00	—	1.004	—	—	—	—
8 30	—	—	—	0.054	—	—
9 30	—	—	0.450	—	—	—
10 00	—	1.004	—	—	—	—
11 00	—	—	—	—	1.647	—
11 45	—	—	—	—	—	0.558
14 30	—	0.990	—	—	—	—
15 30	1.062	—	—	—	—	—
17 00	—	—	—	0.101	—	—
19 00	—	0.962	—	—	—	—
19 30	1.071	—	—	—	—	—
21 00	—	—	—	—	1.623	0.603
23 45	—	—	—	—	—	—
27 00	—	—	—	0.102	—	—
28 00	—	—	0.531	—	—	—
29 00	—	—	—	—	1.602	—
30 00	1.008	—	—	—	—	—
31 00	—	0.927	—	—	—	—

of 1.7 ohms in 24 minutes, and ultimately fell to 0.78 ohms. The variation in r_e was more marked. At first it was 7.3 ohms. The next reading gave 88 ohms. During the recovery readings this resistance was of the same magnitude as at first. We attributed this great variation to some experi-

mental error which had escaped our notice. It is apparent that the internal resistances are of the relative magnitudes 1, 10, and 80. The one to ten ratio could be attributed to the decreased carbon electrode surface and the

TABLE II.

RECOVERY.

Time.	E	E'	E_e	E_e'	E_s	E_s'
min. sec.						
0 30	—	0.972	—	—	—	—
1 00	1.062	—	—	—	—	—
1 15	—	—	—	—	1.656	—
1 30	—	—	−0.522	—	—	—
2 00	—	—	—	−0.279	—	—
2 30	1.098	—	—	—	—	—
3 30	—	1.008	—	—	—	—
4 30	—	—	—	—	1.674	—
5 30	—	—	—	—	—	0.864
7 00	—	—	0.495	—	—	—
7 30	—	—	—	0.279	—	—
9 30	1.152	—	—	—	—	—
11 00	—	1.053	—	—	—	—
13 00	—	—	0.468	—	—	—
15 00	—	—	—	0.270	—	—
16 00	1.170	—	—	—	—	—
16 45	—	—	—	—	1.680	—
17 30	—	—	—	—	—	0.900
26 30	—	1.107	—	—	—	—
27 00	—	—	—	—	1.680	—
27 30	—	—	—	—	—	0.918
28 00	—	—	0.414	—	—	—
28 30	—	—	—	0.243	—	—
29 00	1.224	—	—	—	—	—
29 30	—	—	0.396	—	—	—
30 00	—	1.109	—	—	—	—
77 00	1.242	—	—	—	—	—
77 30	—	1.152	—	—	—	—
78 00	—	—	0.360	—	—	—
78 30	—	—	—	0.243	—	—
79 00	—	—	—	—	1.680	—
79 30	—	—	—	—	—	0.954

insertion of the glass plate. This does not help us in the one to eighty ratio. Now Carhart has shown[1] that the internal resistance varies with the

[1] See previous reference.

current. An introduction of 100 ohms in the main circuit would reduce the current to the same magnitude as the current in the E_c' circuit. To obtain appreciable differences in the readings for E and E' with this resistance in circuit, the connections were changed. The galvanometer was placed in series with 30,000 ohms and the battery. This gave a deflection of 366 scale divisions. When the battery was shunted with 100 ohms, the deflection was 362. This gives an internal resistance of 1.1 ohms, and the ratio is now about $\frac{1}{7}$ to $\frac{1}{7.5}$. With the galvanometer connected in this manner, a readable deflection could be obtained when the E_c series was shunted with one ohm. This gave a deflection of ten scale divisions, but

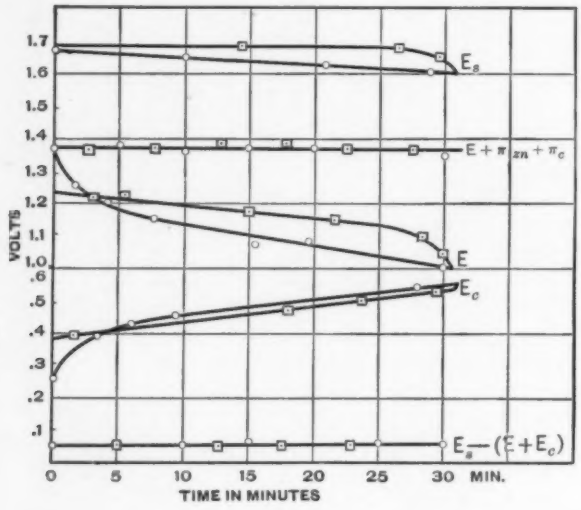


Fig. 2.

it took the series four hours to regain the value first obtained when the battery was upon open circuit, viz., 73 scale divisions. This gives an internal resistance of 6.3 ohms, — a ratio of 1 to 5.5. The current is now, however, three times that in the main circuit with 100 ohms. This difference must be an electrode or contact of electrode and solution phenomena, as the two circuits giving E and E_c are in every respect symmetrical. Streintz[1] has succeeded in measuring the resistance of a cell by means of an alternating current, and finds that the kathode resistance alone shows a dependence upon the current strength, while the anode resistance scarcely varies with the same. As the special carbon is twice kathode in this experiment, the kathode resistance does not help us out. When the main

[1] Wied. Annal., Vol. 57, p. 711, 1896.

carbons are kathode, the internal resistance is smallest, and one would scarcely think that on becoming anode the resistance would be so large. We cannot attribute the difference to polarization, as the difference is marked at the outset when no polarization has occurred.

The chief merit of this method is the means it gives us of determining single potential changes. The curves for E, E_z, and E_c (see Fig. 2) show very decidedly what is taking place. The observations for the polarization are given in the curves by small circles, and the observations for recovery are shown by small squares. It is apparent that the rapid fall of electromotive force at the commencement of a run is to be attributed to polarization at the carbon electrode. Furthermore, the polarization at the zinc electrode cannot be left out of account. The curve shows that the zinc polarization increases uniformly. When the cell is thrown upon open circuit the phenomena are almost exactly reversed. In the first minute of recovery, 18 per cent of the entire loss in electromotive force is regained, and 85 per cent of this gain occurs at the zinc electrode. In five minutes recovery the polarization at the zinc electrode had vanished. The recovery of total electromotive force for the rest of the thirty minutes is due to recovery from polarization at the main carbon electrode. The recovery at the carbon electrode is nearly uniform for thirty minutes. However, the observations are not so decisive as the observations upon the increase of polarization at the zinc electrode. The sum of the observed electromotive force and of the polarization at the two electrodes should be constant and equal to the original electromotive force. We have designated the polarization at the zinc and carbon electrodes by π_{zn} and π_c, respectively, and have drawn a curve showing $E + \pi_{zn} + \pi_c$. This curve is as near a straight line as could be expected. As is apparent, E_z should equal E plus E_c. The curve designated $E_z - (E + E_c)$ shows, however, a constant value equal to 0.054 volts.

Upon the theory of Nernst, we can understand the phenomena here noted. The electromotive force at the zinc electrode is expressed by $\frac{RT}{2\epsilon} \log_e \frac{P}{p}$, where R, T, ϵ, P, and p represent the gas constant, absolute temperature, current required to give the one gram-equivalent of the metals, solution pressure, and osmotic pressure of the zinc ions, respectively. Before a current is generated the quantity p is very small. During the action of the cell, the pressure p of the zinc ions would increase at the zinc electrode, and therefore the electromotive force would fall. The ions would of course be more concentrated in the strata nearest to the zinc electrode. The ion first passing into solution would, in a period of thirty minutes, be less than 2 mm. from the electrode. When the cell is thrown upon open circuit, diffusion of the zinc ions occurs. From the

formula it is apparent that the recovery curve at the zinc electrode should be exponential in character. The observations show that this is probably the case, but the readings of the galvanometer are neither large enough nor frequent enough to demonstrate this character beyond a doubt. At the carbon electrode the gases liberated form a gas battery in opposition to the main circuit. The back electromotive force would increase rather rapidly at first, and later more uniformly. Upon open circuit gas absorption would still continue, and the solution pressure of the gas slowly decrease. It has been shown that the solution pressure of a gas can be expressed by the Nernst formula, and it would scarcely be expected to be as uniform as here noted. However, after standing one hour upon open circuit, the polarization at the main carbon electrode is still apparent, and its magnitude shows that the recovery curve cannot be considered a straight line.

Conclusions.

1. Variation in kathode resistance with current strength does not account for the differences in internal resistance noted in this experiment.

2. Polarization occurs at both electrodes, but is more marked at the carbon electrode.

3. On closing the circuit the rapid fall of electromotive force is due principally to polarization at the carbon electrode.

4. The rapid rise in electromotive force, when a cell is first thrown upon open circuit, is largely due to recovery from polarization at the zinc electrode.

UNIVERSITY OF ILLINOIS, July, 1896.

THE TRACE OF THE GYROSCOPIC PENDULUM.

BY ERNEST MERRITT.

THE gyroscope, in its numerous more or less modified forms, has long been an object of interest to the student of physics. Its erratic movements when disturbed, and its seeming defiance to the laws of gravitation, cannot fail indeed to arouse the curiosity of all who observe it. For this reason, if for no other, the theory of its behavior deserves a clearer and more thorough treatment in works on mechanics than it usually receives.

The principles on which the action of the gyroscope depends find extensive application also in all branches of physics, both pure and applied. In practical engineering they are of importance in connection with high-speed machinery. In the theory of light and magnetism they have led

to Kelvin's hypothesis of a gyroscopic ether, and to an explanation of the magnetic rotation of the plane of polarization. In pure mechanics the gyroscope may be made to give numerous excellent illustrations of general dynamical principles and methods.

Elementary explanations of the behavior of the gyroscope are usually unsatisfactory, either because they are lacking in clearness and completeness, or because they are unsound. Professor Perry's little volume on "Spinning Tops" forms, however, a notable exception to this general statement. The treatment there given, although quite elementary, is so clear and direct, and so suggestive, that it may well be recommended even to advanced students. Much can be accomplished by the straightforward, physical methods adopted by Professor Perry, even without the use of a single formula or mathematical expression; and I think all will agree that such methods, when applicable, are to be preferred to a discussion in which the physical truths are largely disguised by their analytical clothing. For a complete and quantitative discussion of the theory of the gyroscope, recourse must however be had to the methods of analysis. Such a discussion is given by Routh, Thomson and Tait, and others. The only objection to the treatment given to the subject by these authors is that it is unnecessarily hard to read.

It has often been suggested that an advantageous method of explaining the precessional movements of a gyroscope is to consider the latter as a special case of the gyroscopic pendulum. In the ordinary form of gyroscope shown in Fig. 1, the supports serve merely to maintain the center of figure fixed in position. The body may be looked upon as free to move in any manner consistent with the condition that this point shall remain fixed. If everything is perfectly balanced, its center of gravity coincides with the fixed point, and there is no tendency for the axis of rotation to change. But if a weight is attached at the end of the shaft, the center of gravity is displaced, and the instrument becomes a pendulum, whose point of suspension is the center of figure, and whose length depends upon the magnitude of the attached weight. If now a motion of rotation is given to the fly wheel we have a gyroscopic pendulum, whose length in most cases is quite small; and, as soon as the weight is released, the motions of precession and oscillation peculiar to such instruments begin.

Fig. 1.

When the speed of rotation is high it is usually not possible to observe the oscillations of the axis, even when the attention is directed especially to this phenomenon. The theory of the motion shows in fact that these oscillations must be quite rapid as well as of extremely small amplitude. Another fact which makes the oscillations difficult to observe, even by

indirect means, is the unavoidable presence of friction in the supports of the instrument. The frictional damping is in most cases sufficient to reduce the motion to a steady precession within a few seconds after the weight has been released. It is only by using a small speed of rotation, in order to make the gyroscopic action comparatively insignificant, that the true nature of the motion can be seen. But, with suitable conditions, it is possible to show not only the oscillatory character of the motion, but also the fact that the vibrations become more rapid, and die out more quickly, as the speed of the fly wheel is made greater.

If a gyroscopic pendulum of the form shown in Fig. 2 is used, the motion can be more readily observed and studied. The oscillations toward the vertical and back again are of considerable amplitude, while the period may be made so great that the vibrations can be followed by the eye. If such a pendulum is made adjustable in length, it is possible to observe the progressively increasing influence of the rotating fly wheel from the case of a long pendulum, whose behavior is scarcely influenced at all by the gyroscopic action, to the case of an extremely short pendulum, which differs only slightly in its action from the gyroscope shown in Fig. 1. While presenting the theory of the gyroscope to an advanced class during the past year, I constructed such a pendulum by merely attaching the rotating part of an ordinary gyroscope to the end of a brass rod, and suspending the latter by means of a universal joint (*P*, Fig. 2). This simple instrument was found to serve its purpose most satisfactorily. The gyroscopic action could be varied through a considerable range by altering the speed of the fly wheel, while still further variation was obtained by changing the length. The general characteristics of the motion, including the effect of various starting conditions, etc., could be studied by direct observation.

Fig. 2.

With an extremely short pendulum, however, and a high speed of the fly wheel, the motion became too rapid to be readily followed. To obtain a record of the curve described by the pendulum in such cases the photographic traces shown in the accompanying plate were made. I am led to present these results here by the fact that such traces are rarely found in the text-books and treatises.[1] The method of obtaining them was as follows: At the end (*M*) of the pendulum a bit of mirror, about 1 mm. square, was attached by means of wax so as to make an angle of 45° with the vertical. The pendulum was suspended in such a position that during the vibrations

[1] I have been able to find only two such traces, viz., in Thomson and Tait, Vol. 1, Art. 74, and in Perry's "Spinning Tops," p. 57. In both cases, the trace is such as would be obtained when an initial negative precession is imparted. Compare Fig. 6.

of the instrument this mirror should remain within the beam of parallel rays sent out by a large projecting lantern. A small pencil of light was thus reflected by the mirror in the direction of the axis of the gyroscope,[1] and left its trace upon a horizontal photographic plate immediately underneath. The work was of course done in a dark room, and screens were arranged so that light was received only by the mirror, and not by the gyroscope itself. Any fogging which may be observed in the photographs is due to an imperfect adjustment of these screens. In making the exposures the plate was protected by a piece of cardboard until the pendulum had been properly started. The cardboard was then removed, and replaced again after the pendulum had completed five or six oscillations. Whether or not a symmetrical figure would be obtained, such, for example, as that shown in Fig. 4, was largely a matter of chance.

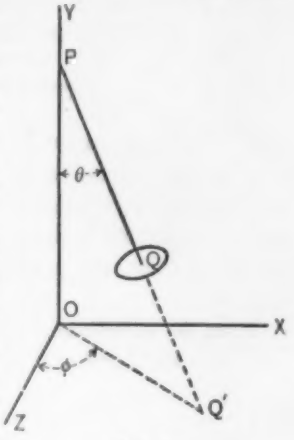


Fig. 3.

Before discussing in detail the various traces shown in the plate, it may be well to refer briefly to the analytical discussion of the gyroscopic pendulum. Let the position of the pendulum be specified by the two angles θ and ϕ, θ being the angle between OY and PQ, while ϕ is the angle between the planes YOZ and OPQ. Let the three principal moments of inertia of the pendulum be B about the axis PQ, and A and C about axes perpendicular to PQ and to each other. Since the instrument is symmetrical about PQ, $A = C$.

We may now apply the general principle that the rate of change of the moment of momentum about any fixed axis is equal to the moment, taken about the same axis, of the force producing this change. Neglecting frictional forces for the present, the only forces to consider are gravity, acting directly downward through the center of mass, and the constraining reactions at the point of support P. Neither of these forces has a moment about either PQ or OY. We conclude therefore (1) that the moment of momentum about OY will be constant, (2) that the angular velocity ω_2 about PQ will also remain unchanged.[2] The first conclusion may be put into mathematical form by making use of the fact that moments of mo-

[1] Owing to the change in direction of PM, the reflected beam does not lie *exactly* in the prolongation of the axis. This fact, together with the changing plane of vibration, has led to the elongated, or elliptical, appearance of some of the traces, *e.g.* Figs. 4 and 9. Since only qualitative results were sought, this distortion seems of small importance.

[2] This conclusion is also dependent on the fact that the inertia axes A and C are equal.

menta, as well as angular velocities, are vector quantities, which can be resolved and combined in the same manner as velocities, forces, etc. The component moments of momenta of the pendulum about the axes PA (in the plane OPQ and perpendicular to PQ), PQ, and PC (perpendicular to the plane OPQ) are readily seen to be: $A\dot{\phi}\sin\theta$, $B\omega_2$, and $A\dot{\theta}$ respectively.[1] The moment of momentum about OY is therefore

$$M_Y = \text{const.} = A\dot{\phi}\sin^2\theta - B\omega_2\cos\theta. \tag{1}$$

By expressing the fact that the rate of change of the angular momentum about PC (not shown in the figure) is equal to the moment of the weight of the pendulum about that axis, we obtain the equation

$$-mgr\sin\theta = A\ddot{\theta} - A\dot{\phi}^2\sin\theta\cos\theta - B\omega_2\dot{\phi}\sin\theta, \tag{2}$$

where r represents the distance between P and the center of gravity.

The derivation of equation (2) by the method indicated is unfortunately complicated by the fact that the axis PC is not fixed. All the necessary equations in fact can be obtained more readily by treating the problem as a case for the application of Lagrange's equations and generalized coördinates.

If ω_1, ω_2, ω_3 represent the component angular velocities about the three principal axes, PA, PB, PC, the kinetic energy is

$$T = \tfrac{1}{2}(A\omega_1^2 + B\omega_2^2 + A\omega_3^2). \tag{3}$$

Although the angular velocities ω_1, ω_2, ω_3 are sufficient to determine the value of T, they do not completely define the *position* of the body, and are therefore not suitable for use as generalized coördinates. Let θ, ϕ, and ψ be chosen as coördinates, θ and ϕ having the same significance as before, while ψ represents the angle between the plane OPQ and some plane fixed in the pendulum and passing through the axis PQ. We then have [2]

$$\left.\begin{aligned} \omega_1 &= -\dot{\phi}\sin\theta\cos\psi + \dot{\theta}\sin\psi \\ \omega_2 &= -\dot{\phi}\cos\theta - \dot{\psi} \\ \omega_3 &= \dot{\phi}\sin\theta\sin\psi + \dot{\theta}\cos\psi \end{aligned}\right\}. \tag{4}$$

[1] A dot placed above a symbol represents differentiation with respect to the time; *e.g.*

$$\dot{\theta} = \frac{d\theta}{dt}, \quad \ddot{\theta} = \frac{d^2\theta}{dt^2}.$$

Note also that a "right-handed" system of axes is used; *i.e.* positive rotation about any axis is right handed to an observer looking along the axis in the positive direction.

[2] "Euler's Geometrical Equations": Routh, Elementary Rigid Dynamics, p. 216.

Equation (3) now becomes

$$T = \tfrac{1}{2} A(\dot\phi^2 \sin^2\theta + \dot\theta^2) + \tfrac{1}{2} B(\dot\phi \cos\theta + \dot\psi)^2, \tag{5}$$

while the potential energy U is

$$U = mgr(1 - \cos\theta). \tag{6}$$

The Lagrangian equations of motion may now be written in the form

$$\frac{d}{dt}\frac{\partial T}{\partial \dot\phi} - \frac{\partial T}{\partial \phi} + \frac{\partial U}{\partial \phi} = 0. \tag{7}$$

Substituting the values of T and U in this equation, and in the corresponding equations for θ and ψ, we obtain:

$$\frac{d}{dt}[A\dot\phi \sin^2\theta + B\cos\theta(\dot\phi\cos\theta + \dot\psi)] = 0; \tag{8}$$

$$A\ddot\theta - A\dot\phi^2 \sin\theta\cos\theta + B(\dot\phi\cos\theta + \dot\psi)\sin\theta + mgr\sin\theta = 0; \tag{9}$$

$$\frac{d}{dt}B(\dot\phi\cos\theta + \dot\psi) = 0. \tag{10}$$

From (10), we see that

$$\dot\phi\cos\theta + \dot\psi = -\omega_2 = \text{const.}$$

Writing $-\omega_2$ in place of $\dot\phi\cos\theta + \dot\psi$ in (8) and (9), these equations become:

$$B\omega_2\cos\theta - A\dot\phi\sin^2\theta = \text{const.}; \tag{11}$$

$$A\ddot\theta - A\dot\phi^2\sin\theta\cos\theta - B\omega_2\dot\phi\sin\theta + mgr\sin\theta = 0; \tag{12}$$

which are the same as equations (1) and (2) above.

The solution of equations (11) and (12) is not easy, even if we confine ourselves to small oscillations about the vertical. But it is possible to determine the main characteristics of the motion without actually solving the equations.

I shall consider, first, the case of zero initial velocity; *i.e.* the pendulum is displaced from the vertical through the angle θ_0, and is then set free. We have, initially, $\dot\theta = 0 = \dot\phi$, and $\theta = \theta_0$. Equation (11) now becomes:

$$B\omega_2(\cos\theta - \cos\theta_0) - A\dot\phi\sin^2\theta = 0. \tag{13}$$

The initial value of $\ddot\theta$ is seen from (12) to be the same as it would be for an ordinary pendulum. The pendulum therefore *starts* to fall toward the vertical. But as soon as θ begins to differ from θ_0, $\dot\phi$ acquires a finite value, which will be positive or negative according to the sign of ω_2. Equation (13) shows that $\dot\phi$ and ω_2 always have the same sign; *i.e.* the direction

of precession is opposite to the direction of rotation of the fly wheel. As the pendulum approaches the vertical, the velocity of precession ($\dot{\phi}$) becomes greater. We see, however, that the pendulum can never pass *through* the vertical, for (13) cannot be satisfied by $\theta = 0$ unless $\omega_2 = 0$. When θ has reached its minimum value it begins to increase again, and, in the absence of friction, will finally reach its original value θ_0. This fact is indicated by equation (12), which shows that, with decreasing θ and increasing $\dot{\phi}$, the acceleration $\ddot{\theta}$ passes through 0 and becomes negative, only to retrace its course when θ has passed its minimum

We may therefore conclude that the motion will consist of a series of oscillations toward the vertical, and back again, accompanied by a variable motion of precession. The greater the velocity of rotation of the fly wheel, the more rapidly will these oscillations take place, as shown by the presence of the term $B\omega_2\dot{\phi}\sin\theta$ in (12). The precessional velocity is zero at the beginning of each oscillation, and reaches a maximum value when θ is least.

The type of motion just considered is illustrated by the traces shown in Figs. 4 and 8, the former trace being taken with a long pendulum, while the latter was made with a pendulum as short as could conveniently be used. The increased influence of the gyroscopic action in the latter case, as indicated by the small amplitude of the vibrations and the short distance between cusps, is well marked. One can readily see that, with a still shorter pendulum, the vibrations might be so small as not to be directly observable. Theory indicates that when ω_2 is large, or r small, the curve should consist of a series of infinitesimal cycloids. The approach to this form is clearly indicated in Fig. 8.

In making the traces shown in Figs. 4 and 8, great care was used to avoid giving any initial velocity to the pendulum. The sharply defined cusps show that the condition of zero initial velocity was very nearly fulfilled. In Fig. 8 the effect of friction, in damping out the vibrations and reducing the motion to one of steady precession, is clearly seen.

If the initial value of $\dot{\phi}$, instead of being zero, is *positive*, the velocity of precession can never become zero. Instead of cusps at the end of each vibration, we shall have a smooth, continuous curve, as shown in Fig. 5. This trace was taken with a rather long pendulum.

The greatest variety of traces may be obtained by making the initial value of $\dot{\phi}$ *negative*. If $\dot{\phi}_0$ has a small negative value, a series of loops is obtained, as shown in Fig. 9. With a somewhat larger value of $\dot{\phi}_0$, these loops are more marked, and the pendulum may even pass through the vertical. Figure 6 shows such a case. If a large negative value is given to $\dot{\phi}_0$, the precession will always remain negative (unless modified by friction), and the trace obtained, like that of Fig. 7, is almost too complicated to follow.

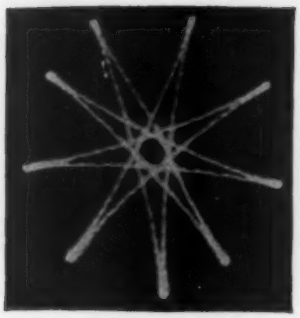


Fig. 4.

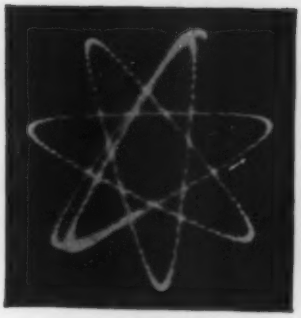


Fig. 5.

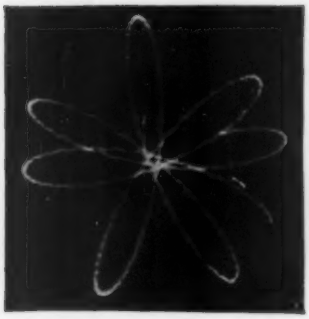


Fig. 6.

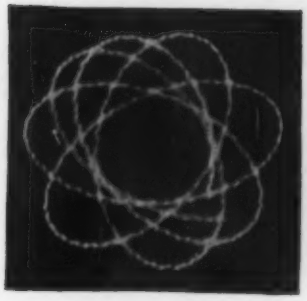


Fig. 7.

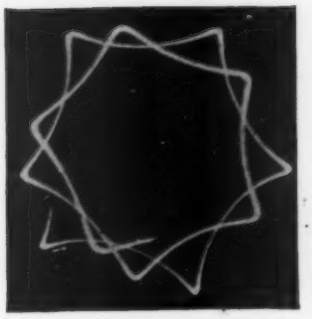


Fig. 8.

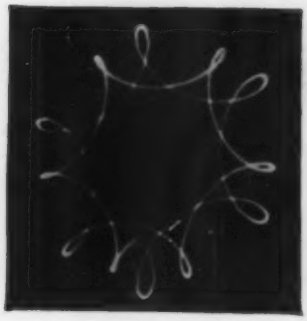


Fig. 9.

MERRITT: GYROSCOPIC PENDULUM.

The effect of friction is shown in Fig. 9, as well as in Fig. 6. In the former curve the loops, at first well marked, gradually become smaller, until finally they are almost reduced to cusps. Doubtless if the trace had been followed still further, these cusps would in turn have been replaced by a smooth curve such as that of Fig. 5. In all cases the effect of friction is to reduce the motion to one of steady precession. This result is accomplished by an *increase* in the velocity of precession. For example, in Fig. 9, the initial negative precession is destroyed, and a positive precessional velocity takes its place. This paradoxical conclusion, that friction may produce an increased velocity, represents only another of the puzzling peculiarities of the gyroscope. The truth of the conclusion can readily be shown if frictional forces are introduced into the equations. But it is not necessary to enter into the analytical treatment in order to reach the result. Bearing in mind the fact that the oscillatory motion is quite rapid as compared with the motion of precession, we see that frictional forces are much more important in the former case than in the latter. The effect of friction in damping out vibrations will be to make the average value of θ smaller; *i.e.* the pendulum approaches the vertical. But when θ diminishes, $\dot{\phi}$ must increase, as shown by equation (11), in order that the moment of momentum about the vertical shall remain constant. So long as the opposition to precession is small compared to the other frictional forces, the results will therefore be as stated above.

Many other features of gyroscopic motion may be studied to advantage by means of traces such as those here shown. If more care were used in obtaining them, I have no doubt that these traces could be made to give a quantitative verification of the theory of such motion. But it is chiefly on account of their value in helping to give a clear and definite interpretation of theoretical conclusions that I have thought it worth while to publish the results contained in this article.

Note on Different Forms of the Entropy Function.

By W. F. Durand.

IT is well known that the heat $\int dQ$ involved in any reversible change in a given substance or system is not independent of the path followed, or in other words of the intermediate conditions passed through. It follows that dQ is not a complete differential, and that $\int dQ$ cannot be expressed as a function of the initial and terminal conditions. As is well known, however, it is possible by means of an integrating factor to reduce dQ to a complete differential, and hence to express its integral thus trans-

formed, as a function of the end conditions. The factor commonly used for this purpose is the reciprocal of the absolute temperature T. We have thus: —

$$\frac{dQ}{T} = d\eta,$$

in which $d\eta$ is a complete differential. The integral η is then termed the entropy, any convenient set of initial conditions being taken from which to measure its value. It is also well known that where one integrating factor, as $\frac{1}{T}$, exists, there will also exist an indefinite number of other factors, leading to a corresponding indefinite series of values of the complete integral.

It is the purpose of the present note to show some of the forms which the integrating factors may take in the case of a perfect gas, as well as the resultant forms of the entropy function, η.

To this end let β denote any integrating factor, and η the corresponding value of the entropy function. We shall then have

$$\int \beta dQ = \eta.$$

It will be noted that the function η thus defined is the general value for any integrating factor β, the common value resulting when $\beta = 1 \div T$. We here, therefore, use the symbol in a general sense, of which the common use is a particular instance.

We shall also find it convenient to assume an auxiliary function P which shall be constant in value for a change involving no inflow or outflow of heat. The function P is therefore constant under the same conditions as η, and each may therefore be expressed as a function of the other. For the purpose in view, P may be entirely unlimited so long as the above condition is fulfilled. In order, however, to fix our ideas, and with no loss of generality, we may take P as a function of the independent variables defining the condition of the system, such that $P = constant$ shall be the general equation to the family of isentropic loci, such equation being expressed in its simplest form. This is still indefinite since many forms may be given to this equation with but slight difference in simplicity. Any one form, however, will answer, and no matter what form be chosen, the general result will be the same. With the language used above, the definition of P holds for any number of independent variables. Where they are more than two, however, space of more than three dimensions is required, and hypergeometrical concepts and terminology must be introduced. For the present purpose, however, it will be quite sufficient to limit our considera-

tion to two independent variables which we shall prefer to take as pressure and volume, denoted by p and v.

Using the auxiliary variable P, we may put in general for any reversible change —

$$dQ = \frac{\partial Q}{\partial P} dP. \tag{1}$$

But $\frac{\partial Q}{\partial P}$ is completely determinate at each point and depends on the properties of the body. It must, therefore, be expressible as a function of p and v. Let us for convenience, as will be seen later, put $\frac{\partial Q}{\partial P}$ in the form

$$\frac{\partial Q}{\partial P} = f(pv) F(P). \tag{2}$$

In this expression the form of the function F is entirely unlimited, while that of the function f will result from that taken for F. We shall have, therefore, from (1) and (2) —

$$\frac{dQ}{f(pv)} = F(P) dP. \tag{3}$$

Now $d\eta$ is by definition a complete differential, and from the relation between P and η, dP must be such likewise. Hence $F(P)dP$ will be a complete differential, and hence, likewise, $\frac{dQ}{f(pv)}$. The same conclusion might also be reached by remembering that P may be defined simply as a function of the coördinates fulfilling certain conditions as above specified, and hence $F(P)dP$ must be a complete differential.

It follows that $\frac{1}{f(pv)}$ is an integrating factor, and we may put —

$$\frac{dQ}{f(pv)} = F(P) dP = d\eta. \tag{4}$$

Remembering that the function F is unlimited in form, it is plain that $\frac{1}{f(pv)}$, $d\eta$, and η may have an indefinite number of values, and in particular that multiplication of the first two members of (4) by P, or by any function of P, will not affect the existence of the general entropy function η. Hence if any particular quantity represented by $\frac{1}{f(pv)}$ or by β is an integrating factor, then the same quantity multiplied by P, by any function of P, by η, or by any function of η, will be an integrating factor also.

From (4) we have for the general value of the series of integrating factors —

$$\beta = F(P) \frac{\partial P}{\partial Q}. \tag{5}$$

While for the similar general value of the series of entropy functions we have —

$$\eta = \int F(P)\,dP. \tag{6}$$

In both of these it will be remembered that the function F is entirely unlimited in form.

It follows that we may also write —

$$\eta = \theta(P), \tag{7}$$

where θ is any function unlimited in form. Again, P may be taken as a special value of η which we may denote by η_1. We may therefore write —

$$\eta = \theta(\eta_1). \tag{8}$$

Let us now express the above general value of β in terms of other differential coefficients. We first note that at any given point, or in any given condition, $\frac{\partial Q}{\partial P}$ is independent of the path or direction of change.

Let us then, as a matter of convenience, take $\frac{\partial Q}{\partial P}$ for constant pressure. Denoting this by $\frac{\partial Q}{\partial P}\Big)_p$ and others similarly we have —

$$\frac{\partial Q}{\partial P}\Big)_p = \frac{\partial Q}{\partial T}\Big)_p \frac{\partial T}{\partial v}\Big)_p \frac{\partial v}{\partial P}\Big)_p = f(pv)F(P),$$

or

$$\beta = \frac{F(P)}{\frac{\partial Q}{\partial T}\Big)_p \frac{\partial T}{\partial v}\Big)_p \frac{\partial v}{\partial P}\Big)_p}.$$

Now let us apply these expressions to a perfect gas, defined as a substance fulfilling the condition —

$$\frac{pv}{T} = \text{constant} = R.$$

For the function P in this case we shall have pv^γ, the well-known equation to the isentropic lines being $pv^\gamma = \text{constant}$. Hence —

$$\frac{\partial Q}{\partial T}\Big)_p = \text{specific heat at constant pressure} = \sigma_p,$$

$$\frac{\partial T}{\partial v}\Big)_p = \frac{p}{R},$$

$$\frac{\partial v}{\partial P}\Big)_p = \frac{1}{\gamma p v^{\gamma-1}}.$$

Hence, reducing, we have —

$$\frac{\partial Q}{\partial P} = \frac{\sigma_v T}{P} \text{ and } \beta = \frac{PF(P)}{\sigma_v T}.$$

This is the general form of the integrating factor for a perfect gas with this particular value of P. For the general value of η we have as in (6),

$$\eta = \int F(P)\,dP.$$

We may now briefly discuss these values.

Let $F(P) = \frac{\sigma_v}{P}$. Then $\beta = \frac{1}{T}$, and we have the usual integrating factor. For the entropy we have —

$$\eta = \int \sigma_v \frac{dP}{P} = \sigma_v \log P = \sigma_v \log (pv^\gamma).$$

Next let $$F(P) = \frac{\sigma_v}{R}.$$

Then $$\beta = v^{\gamma-1}, \text{ and } \eta = \frac{\sigma_v}{R} P = T\sigma_v v^{\gamma-1}.$$

Again let $$F(P) = \frac{\sigma_v P^{\left(\frac{1}{\gamma}-1\right)}}{R}.$$

Then $$\beta = p^{\frac{1}{\gamma}-1},$$

and $$\eta = \frac{\gamma\sigma_v P^{\frac{1}{\gamma}}}{R} = \gamma T\sigma_v p^{\left(\frac{1}{\gamma}-1\right)}.$$

The second and third forms are of interest as showing that an integrating factor may be found expressed simply as a function of v, and one expressed simply as a function of p.

It will be noted that $v^{\gamma-1}$ and $p^{\frac{1}{\gamma}-1}$ are integrating factors for a perfect gas only, and that for other substances, or systems, factors similarly found would have different values. In this connection it may not be without interest to note in closing that $\frac{1}{T}$ is an integrating factor for all substances or systems simply because it is so defined, and it is possible thus to have an integrating factor common in form for all substances, because the quantitative definition of temperature is not previously required, and we are therefore at liberty to choose the nature of the unit and scale in accordance with this purpose. We cannot have $v^{\gamma-1}$, or any other function of v, an integrating factor for all substances, because we are not at liberty to choose an arbitrary scale of volume such that this condition shall be fulfilled. Volume and its measure are geometrical concepts, and are fixed by considerations antecedent to the problems of thermodynamics. Similar considerations show that no function of p alone can be an integrating factor for all substances. It may also be noted that while $1 \div T$ is an integrating factor for all substances, the expression of its value as a function of p and v will vary according to the substance.

NEW BOOKS.

Physikalische Technik. By F. FRICK. Sixth edition, revised by O. LEHMANN. Two volumes, large 8vo, pp. 725 and 1054, respectively. Braunschweig, Viewig und Sohn, 1895.

Frick's *Physikalische Technik* is one of the earliest of the books intended to assist the lecturer on physics in the preparation of illustrative experiments. Written by the director of the Hochschule of Freiburg about the middle of this century, at a time when the value of experimental work and concrete methods of instruction was only beginning to be generally appreciated, its usefulness was quickly recognized, and in 1862 the second edition was translated into English. Since that time the same field has been covered, in whole or in part, by such books as Weinhold's *Physikalische Demonstrationen*, and Lehmann's *Physikalische Technik*, in Germany, and Dolbear's *The Art of Projection*, Wright's *Light*, and Tyndall's *Lectures*, in England and America.

The work before us, now in its sixth edition, still remains, however, the most ambitious, as well as the most complete, of its kind. While the general plan of the earlier editions has been retained, Dr. Lehmann has added greatly to the amount of material presented, and has subjected the whole to a thorough revision. Instead of a book of less than 500 pages we now have two large volumes, one of which alone is twice as large as the original work.

The first volume begins with a consideration of the best arrangement for the lecture room, apparatus cabinets, and work shop. In this chapter various fixed accessories are also discussed. Then follow directions for cleaning and repairing apparatus, for lacquering, cementing, blowing and cutting glass, and for working such materials as cork and rubber. This chapter, which occupies about 80 pages, contains a vast amount of useful information about mechanical and physical manipulations of all kinds.

The detailed description of lecture experiments begins with the second part of Vol. I., which takes up the subjects of statics (solids, liquids, and gases), heat, and dynamics and thermodynamics, in the order here given. The experiments are almost without exception of an illustrative character consistent with the general plan of the book, and are described in a direct and practical manner. The arrangement of subjects and experiments, however, leaves much to be desired. In most cases the number of

experiments under each head is far in excess of what could be presented during any ordinary lecture course. This is not true, however, in the case of surface tension and capillarity. These two subjects, which Boys has shown to be capable of such fascinating experimental illustration, are treated with a briefness quite out of keeping with the rest of the book.

It is in the second volume, and especially in that part which deals with the subjects of electricity and magnetism, that the changes made by Dr. Lehmann are most radical. In the new material added we find references to the most recent developments of electrical science: for example, to such subjects as Tesla's high frequency phenomena, Hertz waves, the discharge of negative electricity by light, kathode rays, etc. It is not possible to treat all of these subjects in detail, even in a book as large as Frick's *Physikalische Technik*. In fact, the directions given for the preparation of experiments are only in a few cases sufficient for actual use. They will nevertheless serve as valuable suggestions, while the references to original articles, which are in most cases given, will help in the preparation of special lectures.

From the American standpoint the editor's attempt to modernize the chapters dealing with electricity can hardly be looked upon as successful. The experiments relating to dynamo electric machinery, and the discussion of electrical measuring instruments for lecture purposes, are especially unsatisfactory. In some cases the methods and apparatus might almost be referred to as antiquated. This is perhaps to be explained by the fact that in this country, much more than in Germany, the teaching of electricity as a branch of physics, and its presentation as a basis for the education of the electrical engineer, have gone hand in hand. Both the science and the art have benefited by this arrangement. The teacher and the investigator have gained the use of instruments and methods perfected by the engineer; while they in turn have contributed to the general stock of engineering data the results of investigations of the highest practical importance. There is little evidence of this union of the pure and applied science in the work before us. In the chapters on current electricity and magnetism the methods and apparatus are practically those of ten or fifteen years ago. It is hardly to be expected, therefore, that this portion of the book will prove of much value in this country. On the other hand those chapters which deal with statical electricity, and with other branches of the subject not yet generally applied in practice, are more extensive, as well as more satisfactory, than any similar treatment in English. Dozens of interesting and important experiments are here described which rarely find their way into our English or American text-books. It can hardly be denied that the tendency in this country is often to give prominence to the practical side of electricity at the expense of those portions of the subject whose practical utility can now be only dimly seen. There results a distorted

presentation of the subject which is as harmful to the engineer as it is to the development of the science. The work of Dr. Frick offers suggestions in regard to these neglected branches which will be of considerable assistance to a lecturer desirous of presenting a well-rounded course.

Throughout the work, and especially in the second volume, considerable space is given to a presentation of general theory. Such discussions, of necessity incomplete, seem to me entirely out of place in a work intended primarily as a help in the preparation of experimental lectures. For the lecturer who knows his subject, they are unnecessary; for one whose preparation is insufficient, they are too brief to be of any assistance. In my opinion such discussions serve merely to increase the bulkiness of the work, and thus to diminish its usefulness.

Like so many of the recent books on scientific subjects, this new edition of the *Physikalische Technik* shows unmistakable evidence of having been written with the shears and paste pot. From the very nature of the task we can expect nothing else. The gathering together of such a mass of useful material from its concealment in the enormous periodical literature of physics, is a task that would well deserve our thanks, even if the author and editor had not contributed a single new sentence. But the reader has a right to expect a logical and convenient arrangement of the materials; and this is *not* found in the work before us. The arrangement of subjects and experiments in the second volume is simply bad beyond all description. A fairly complete index does indeed make it possible to find the description of an instrument whose exact name is known, or of some branch of physics that can be specified by a definite title. But the reader who hopes to find the experiments dealing with related subjects grouped together, so that suggestions may be quickly gained by merely glancing them over, will be grievously disappointed. For example: A lecturer desiring information regarding the Lichtenberg figures and allied phenomena would, I think, naturally look in Section O of Volume 2, which is entitled "Elektrische Staub- und Lichtfiguren." His search for Lichtenberg's figures would indeed be successful, but the related phenomena of dust figures and breath phantoms would escape him; for these subjects, widely separated from one another, are included in a preceding chapter on the "Durchgang von Elektricität durch schlechte Leiter." The subject of breath phantoms is especially well concealed, being directly preceded by the description of tubes for the development of ozone, and followed by a discussion of oil condensers. Except the one topic, Lichtenberg figures, Section O, contains nothing that could properly be classified under the title "Staub- und Lichtfiguren." Among the subjects that it *does* contain may be mentioned the action of a magnetic field on the spark discharge, the electric furnace, Crookes' tubes, and the electric arc. Similar instances of bad

arrangement might be cited almost without limit. The material contained in the book will undoubtedly prove of great value, in spite of the manner in which it is arranged. But it is unfortunate that the opportunity of accomplishing much more than this has not been utilized.

ERNEST MERRITT.

Submarine Cable Laying and Repairing. By H. D. WILKINSON, M.I.E.E. pp. 406. Just published. New York, D. Van Nostrand Company, 23 Murray Street. London, Electrician Printing and Publishing Company, Limited.

This book contains a very full description of methods of laying and repairing submarine cables, and the author has evidently added a number of sketches and photographs of his own, taken during such operations. The book is divided into four main chapters, the first of which is devoted to the operations performed by cable ships, the second to cable ships themselves, the third to methods of localizing faults in submarine cables, and the fourth to the laying of submarine cables. The book abounds in just such practical information upon this interesting and important subject as it is almost impossible to find in other publications with which we are acquainted. The subject-matter is well illustrated by 219 cuts, and the practical side of the subject has received very full treatment. An excellent index is supplied for the illustrations as well as for the topics discussed. The book is addressed to all those who are interested in the subject of submarine telegraphy, and as such it is well calculated for use in general libraries. It is also designed to be of great use to those who are interested in submarine telegraphy from a technical point of view, since it not only contains much information which is very useful for reference, but also gives the student a clear insight into the leading principles dealt with. We believe the book will be very cordially received, as it is the only one we know which deals with its subject in a simple, interesting, and thorough way.

A. E. K.

Physikalische-Chemische Propaedeutik unter besonderer Berücksichtigung der medicinischen Wissenschaften, und mit historischen und biographischen Angaben. By Dr. H. GRIESBACH. Vols. I. and II. Leipzig, Wilhelm Engelmann, 1895–96.

This book attempts the difficult task of bringing together the essential truths in our knowledge of nature on its animate as well as its inanimate side. In other words, it professes to be a compendium of all that is funda-

mentally important in the physical, chemical, and biological sciences. The author has evidently read widely in the entire literature of the natural sciences, and has succeeded in condensing into small compass a great amount of useful and interesting information which in the main seems to be reliable. The special aim of the book apparently is to furnish students of the biological or medical sciences with brief descriptions of physical conceptions in regard to the nature and properties of matter and energy, and so far as possible to illustrate the value of these conceptions in the study of living processes. It contains many concise definitions which will be useful to those whose knowledge of physics is incomplete. For the most part, also, the descriptions are not technical and may be followed easily by the non-scientific reader. The book seems therefore to be well adapted to the needs of those who desire simply intelligible statements of accepted scientific beliefs, and do not care for elaborate expositions or scientific proofs. Necessarily it covers a very wide range of subjects. Indeed the extremely miscellaneous character of the subjects treated prevents the book from being readable as a whole, and lays it open to the objection of being merely an *omnium gatherum* of things scientific without any very serious educational purpose. For purposes of reference it may be regarded as a handy volume, particularly for students of biology or medicine, and also, as the author suggests in his announcement, for lawyers who come into occasional professional contact with scientific matters. A valuable feature for the specialist is the long list of references to standard treatises, and the numerous biographical sketches scattered throughout the book. It is to be hoped that when completed the book will contain an index that shall enable the reader to avail himself readily of this material.

W. H. HOWELL.

Physical Measurements. By FRANK C. WELDON. 8vo. pp. 232. London, Gill & Sons, 1895.

This little book is intended as a manual of laboratory practice for students in the secondary schools. The experiments described in this volume deal with the mechanics of solids, liquids, and gases, a great deal of space being devoted to simple geometrical measurements, such as the determination of area and volume. Most of the apparatus required is of extreme simplicity, and the experiments are of the elementary character suited to the grade of students for which the book is intended. The author's plan of instruction will be best stated by a quotation from the preface: "The pupil should be led to regard the work in the physical laboratory as a systematic series of experiments by means of which he will discover for himself scientific truths."

E. M.